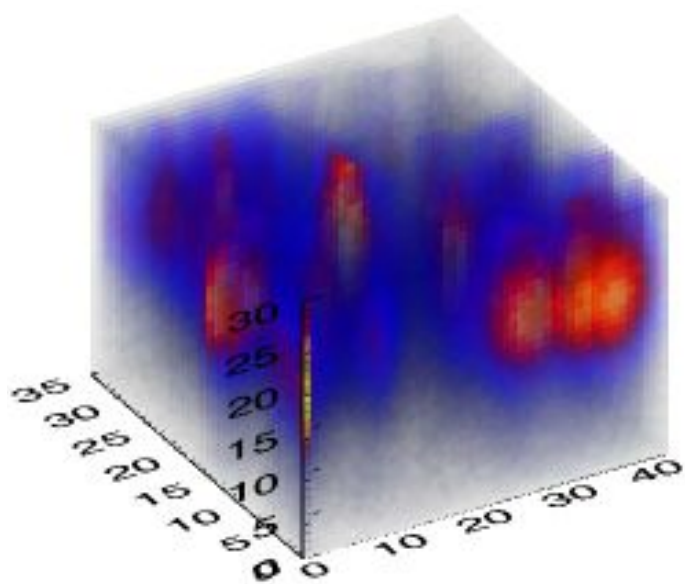


# **CHEMICAL REACTIVITY IN SOIL MICROSITES**

## **The Need for Rapid, High-Resolution, Multi-Element Synchrotron X-ray Capabilities**

**Dean Hesterberg, Montserrat Fuentes, Matthew Polizzotto**  
Departments of Soil Science and Statistics, NC State University



### **COLLABORATORS**

**Ryan Tappero and Paul Northrup (NSLS)**  
**Ian McNulty (APS)**  
**Juergen Thieme (NSLS-II)**

**ROCK & CELL – EARLY SCIENCE WORKSHOP NSLS-II**

# COMPETING DEMANDS ON OUR SOIL RESOURCES

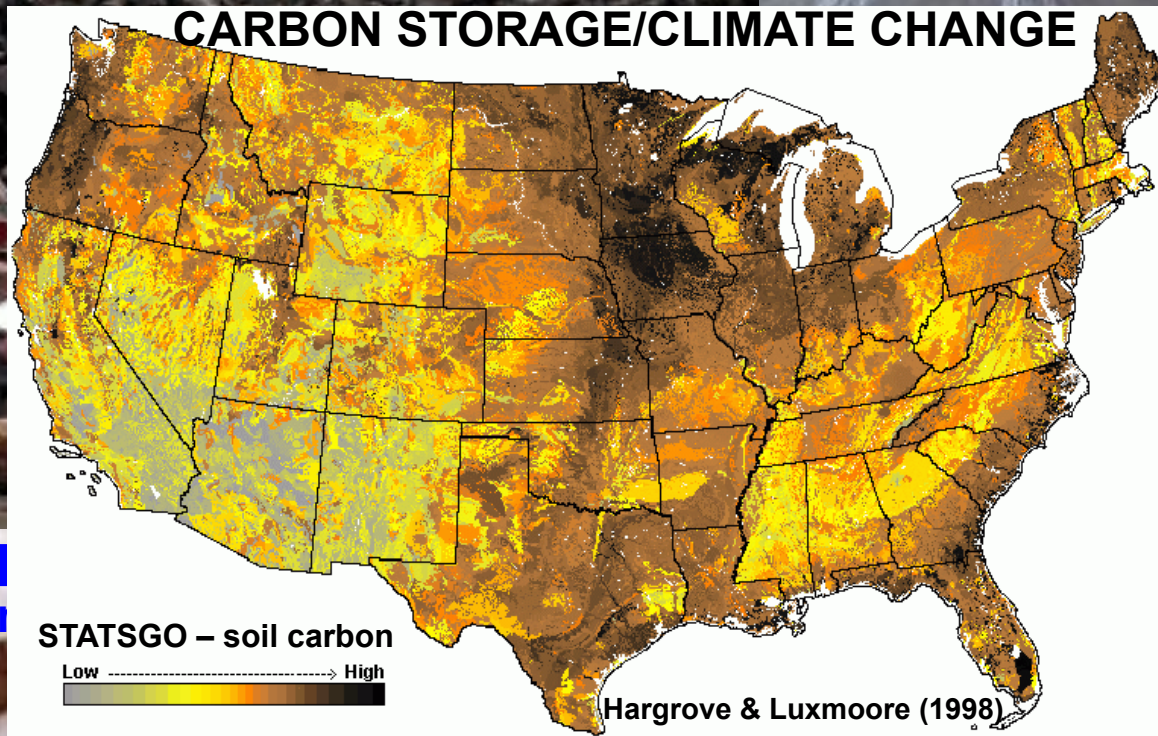
FOOD SECURITY

ENERGY PRODUCTION

TOXIC AND NUCLEAR  
WASTE MANAGEMENT

WASTE MANAGEMENT

CARBON STORAGE/CLIMATE CHANGE



HUMAN HEALTH  
(arsenic poisoning in

QUALITY  
TION  
(Neuse River)

TVA Kingston, TN (2008)

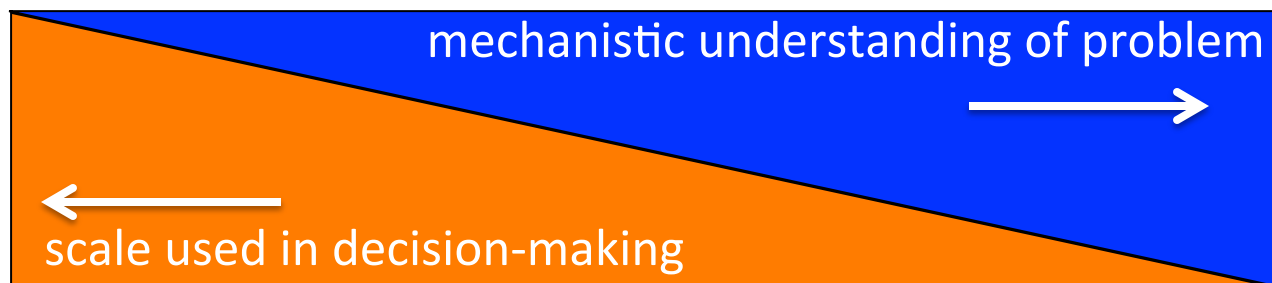
clas.ufl.edu

1 billion gallon coal fly ash spill

source: sea.net



# MOLECULAR ENVIRONMENTAL CHEMISTRY AND LAND MANAGEMENT



kilometer

meter

millimeter

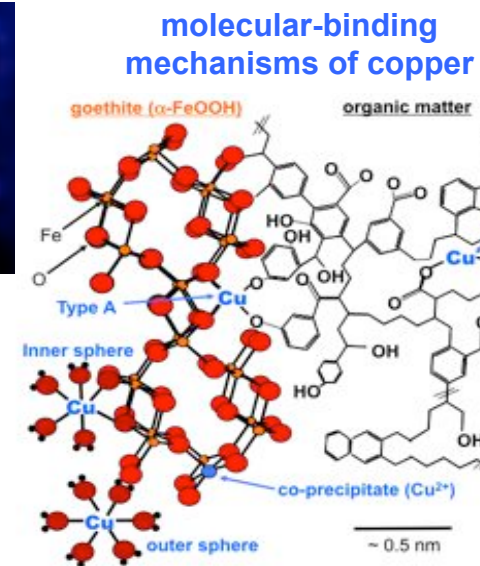
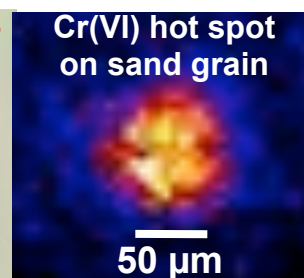
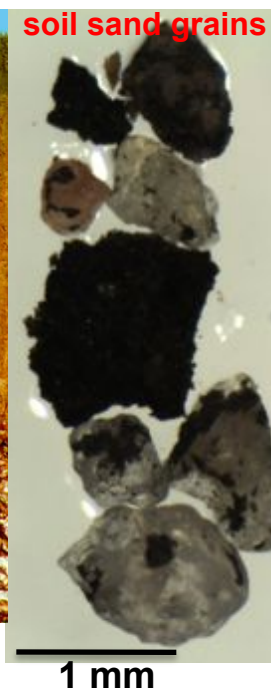
micrometer

nanometer



communitybridge.blogspot.com

energy production  
toxic waste management  
precision agriculture



soil classification

reactive chemical transport modeling

Knowledge transfer?

# OBJECTIVE

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**Illustrate limitations and opportunities for applying synchrotron x-ray micro/nanoprobes to soil materials.**

# **CHEMICAL REACTIVITY IN SOIL MICROSITES**

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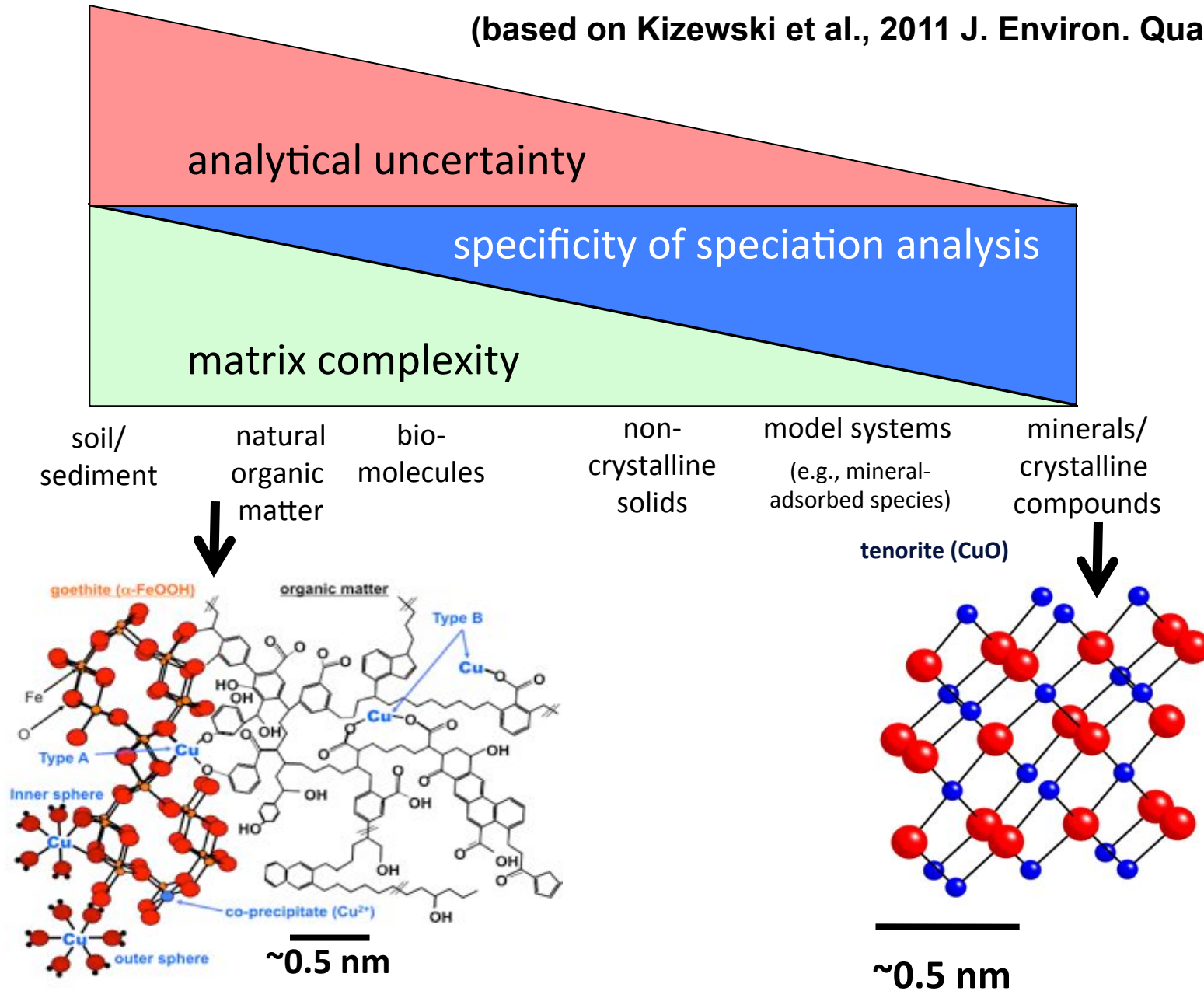
- **The Chemical Speciation Model**
- **The Reactive Microsite Model**
- **Measuring Soil Reactivity**

# The Chemical Speciation Model



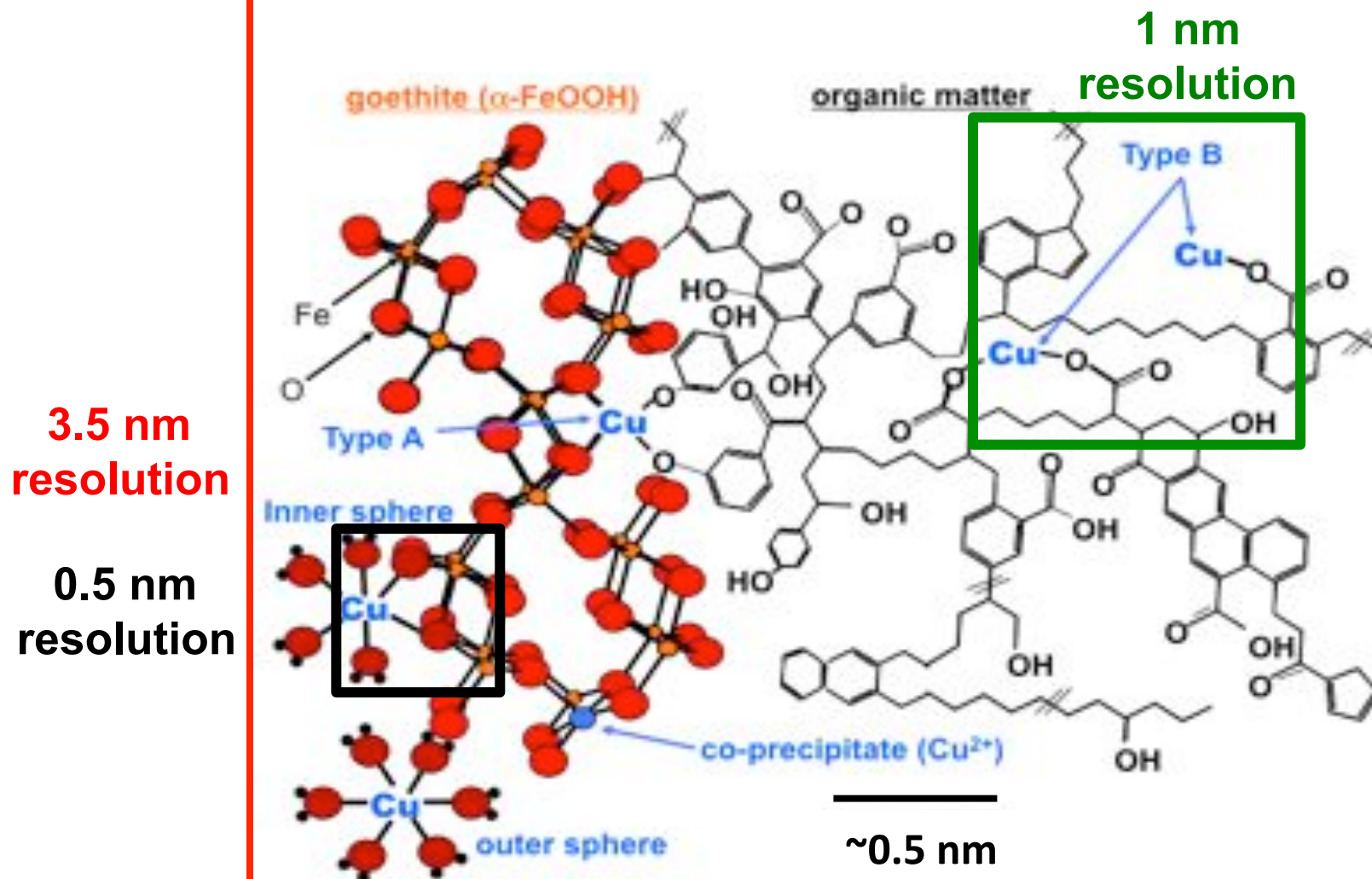
# SOIL COMPLEXITY AND ANALYTICAL SPECIFICITY

(based on Kizewski et al., 2011 J. Environ. Qual. 40:751)





# ANALYTICAL SPECIFICITY



(based on Hesterberg et al., 2011 J. Environ. Qual. 40:667)



**Those are species found in different model systems, but how many different chemical species of an element are in a given soil?**

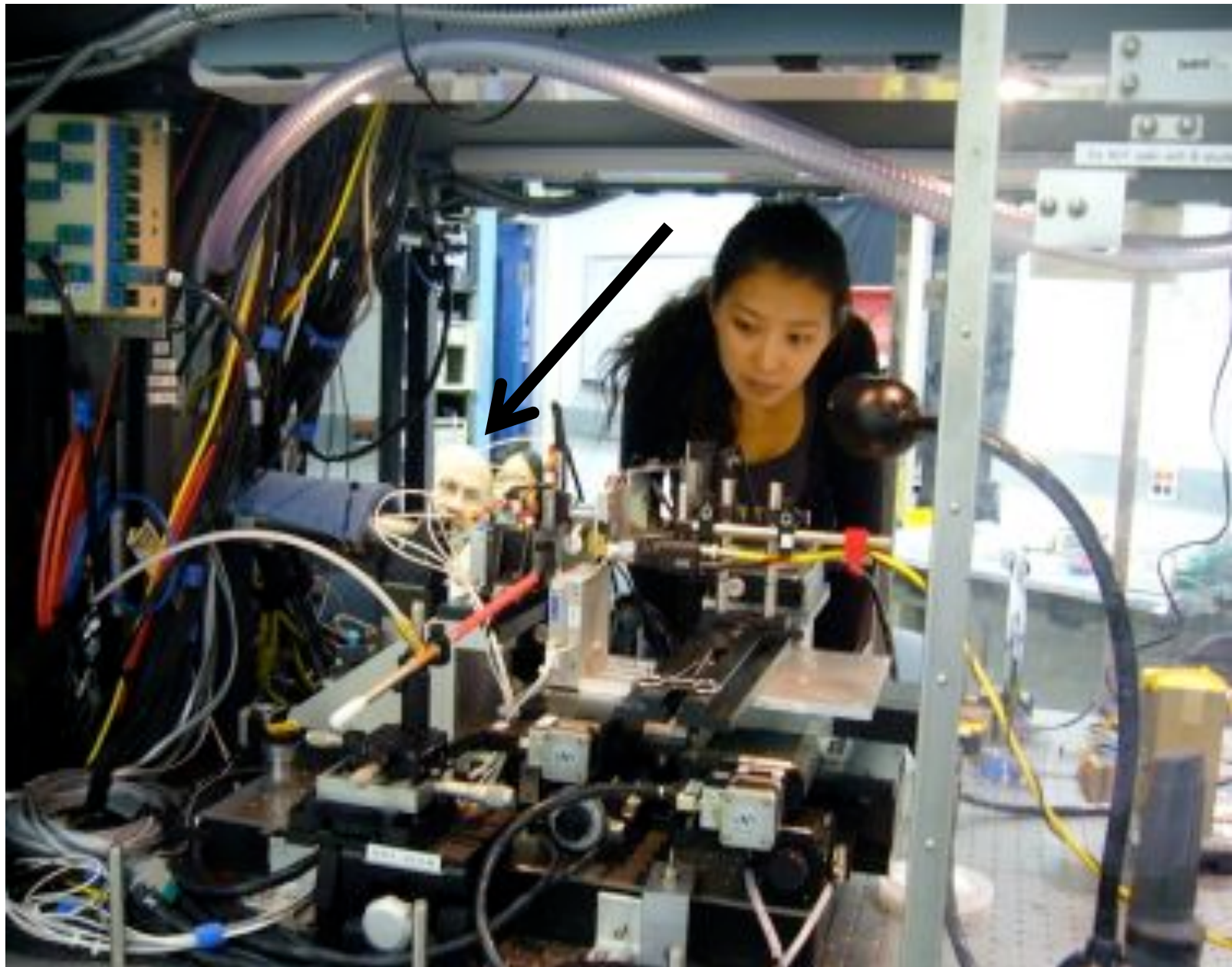
**PHOSPHORUS EXAMPLE**

# Balancing Phosphorus Nutrition and Water Quality

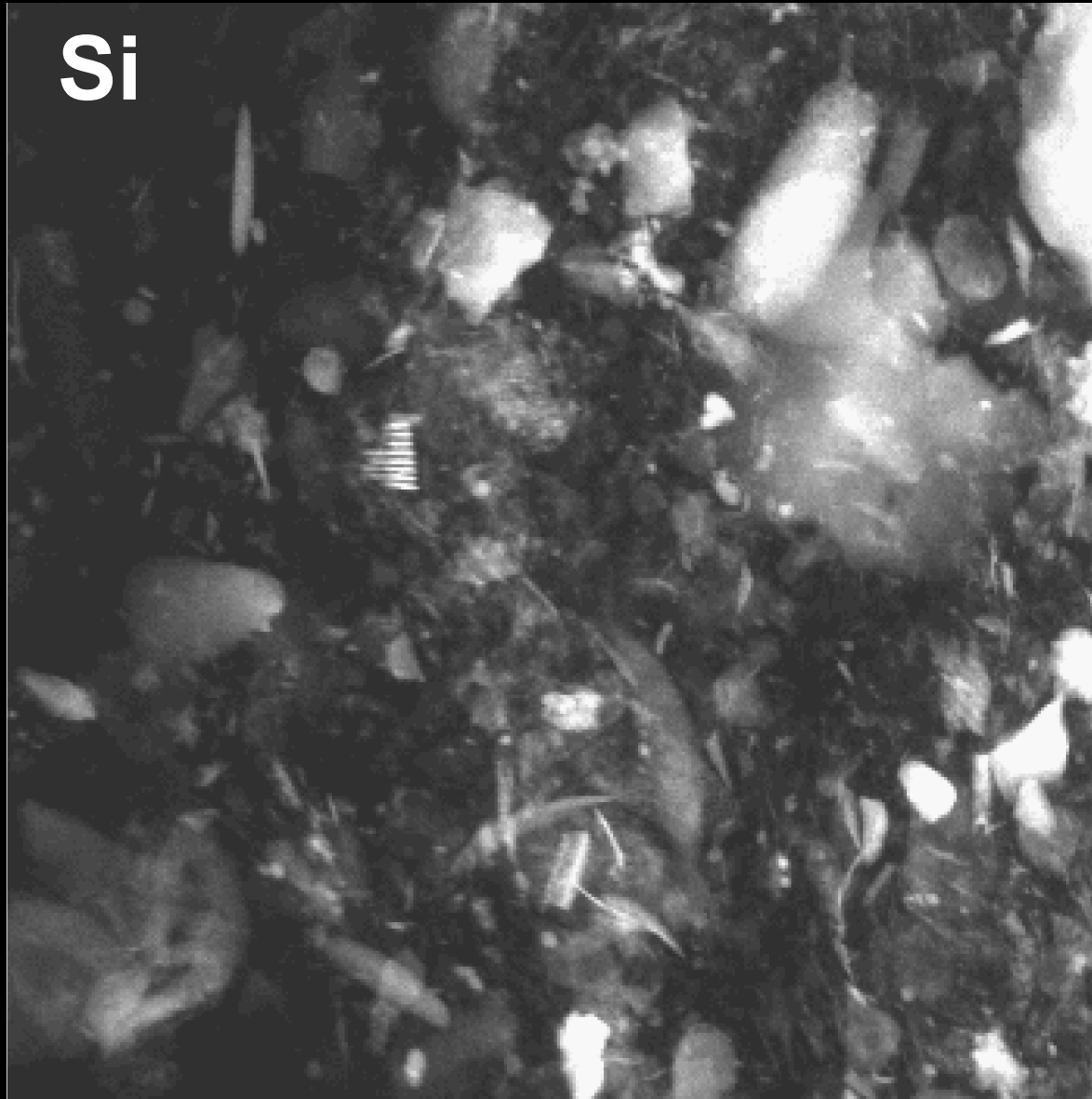


(from USDA-NRCS image bank)

# APS Sector 2-ID-B X-ray Microscope



## Silicon Map – Organic Soil Sample from North Carolina

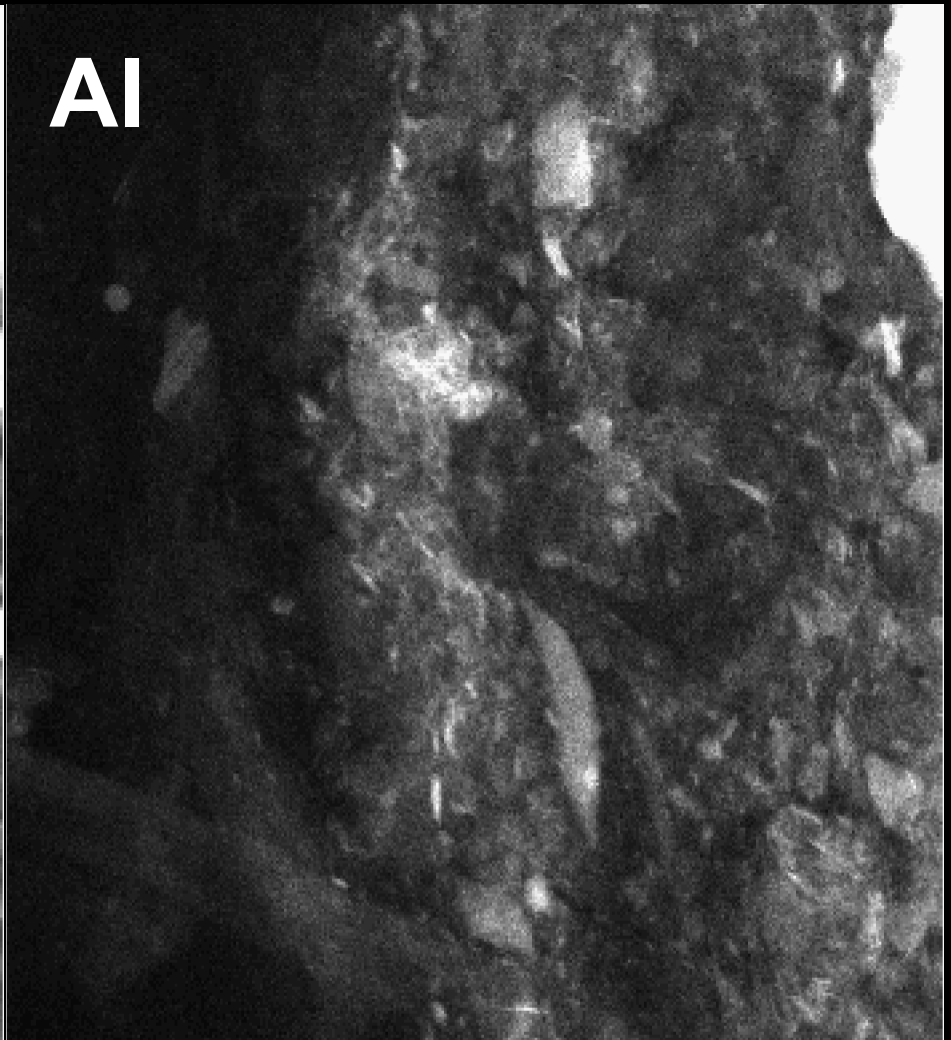
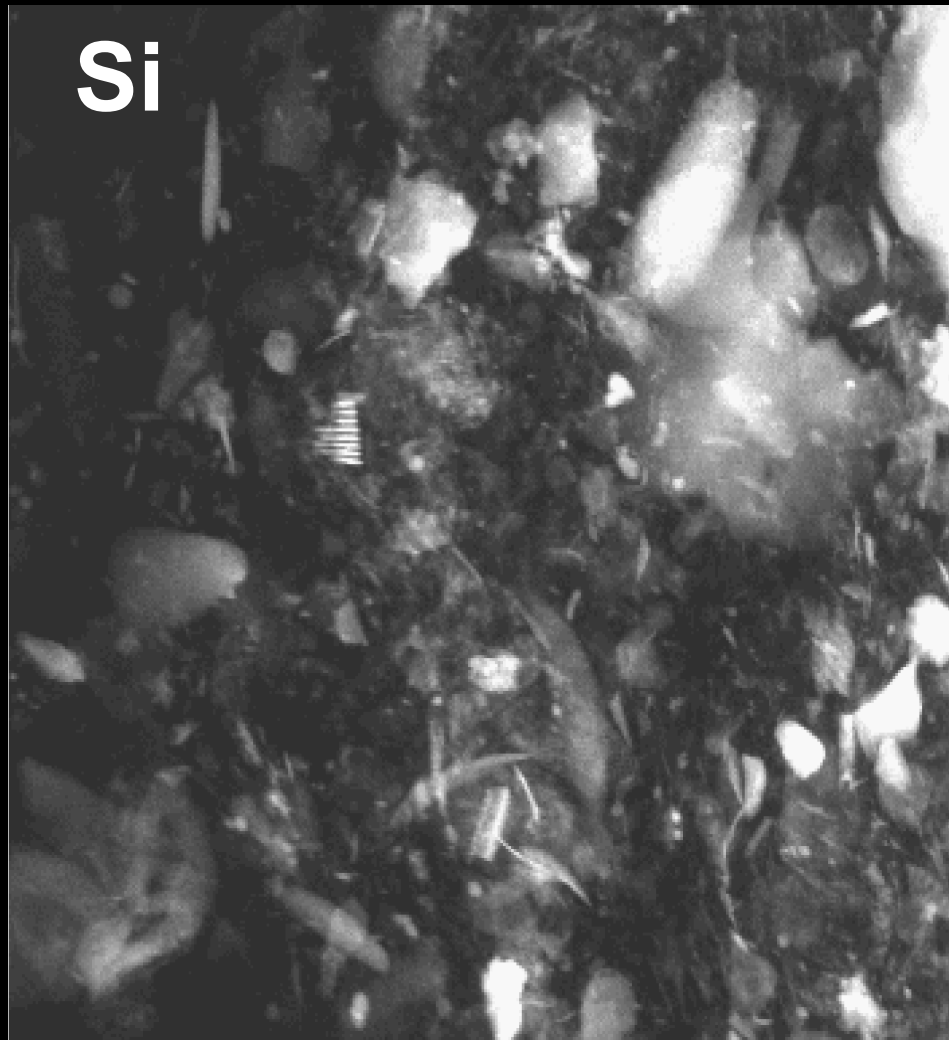


**50  $\mu\text{m}$**

**(30 nm  
spot size)**

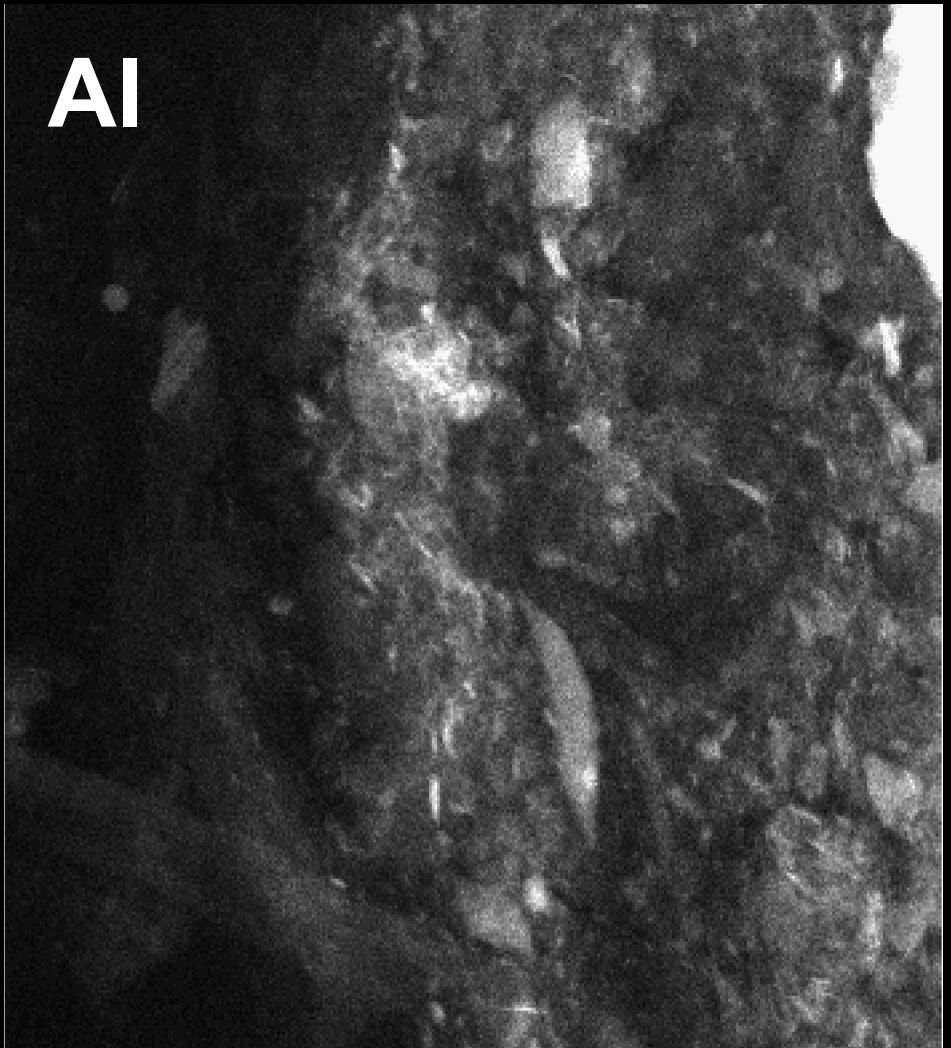
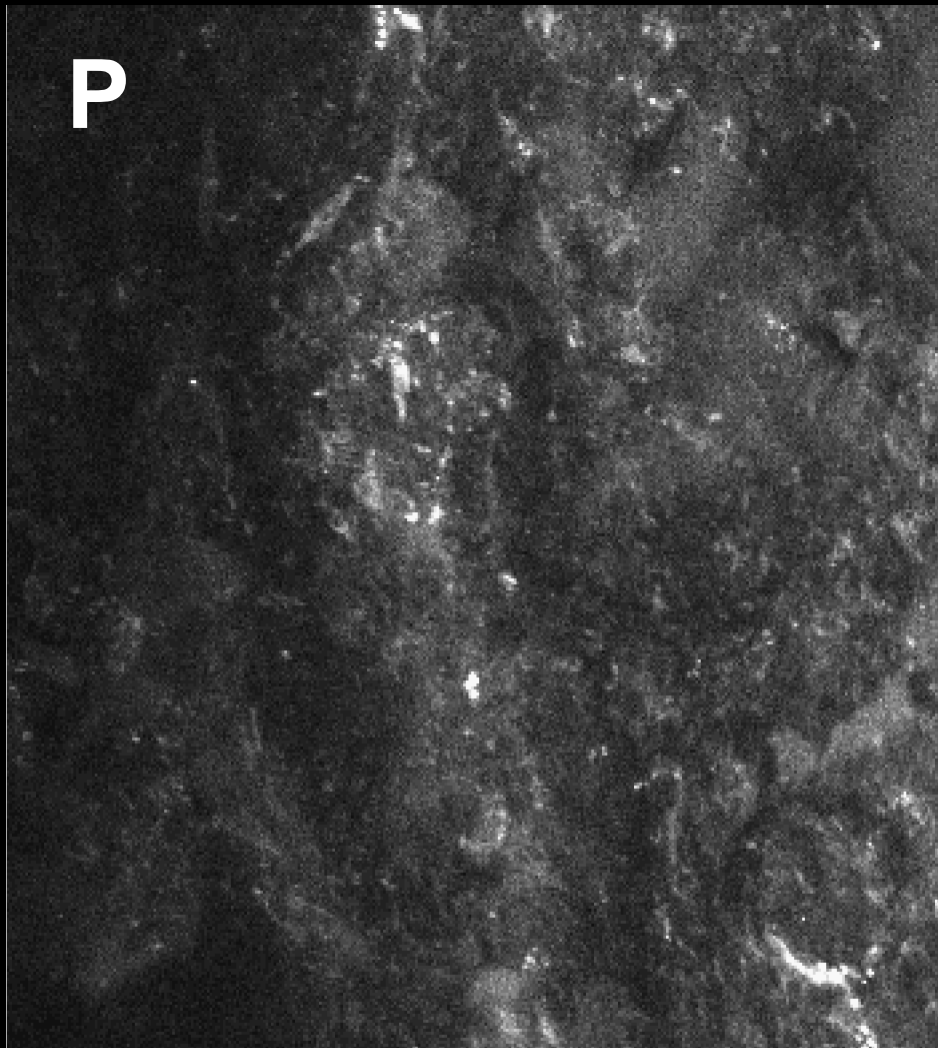


# SILICON AND ALUMINUM MAPS



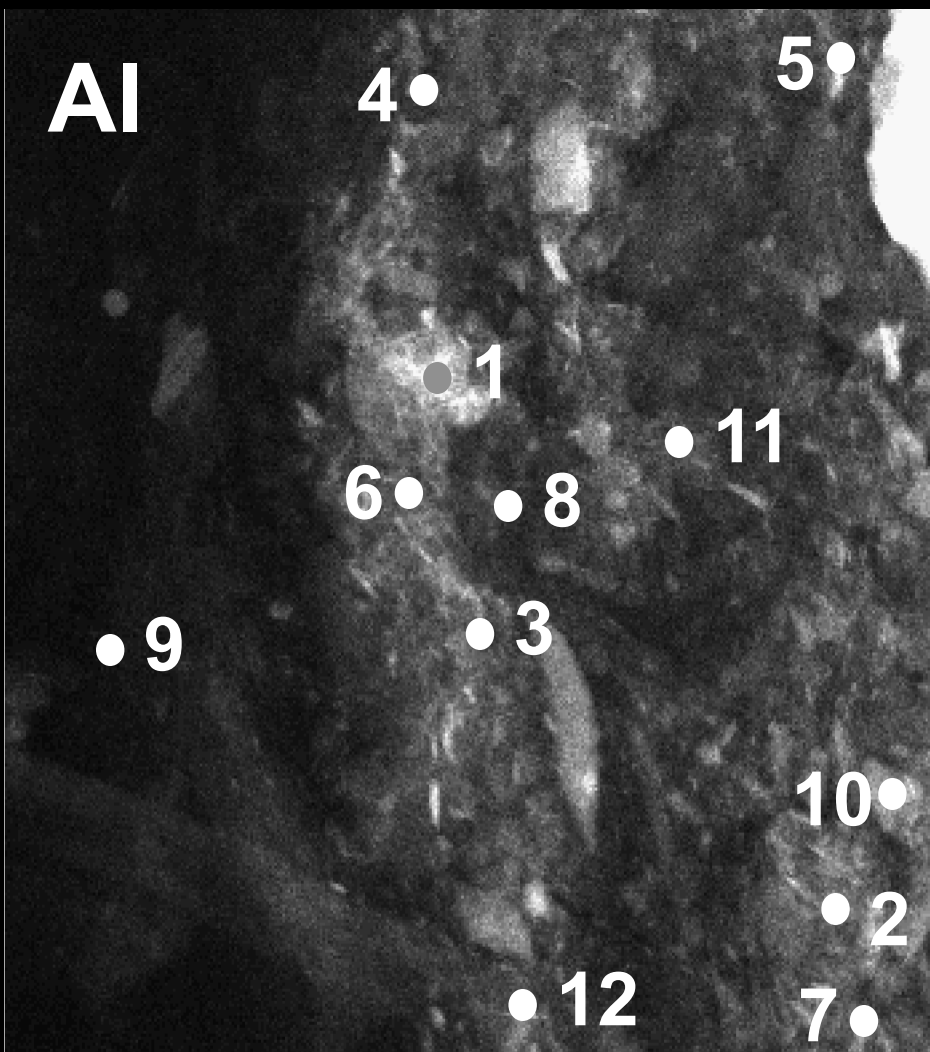
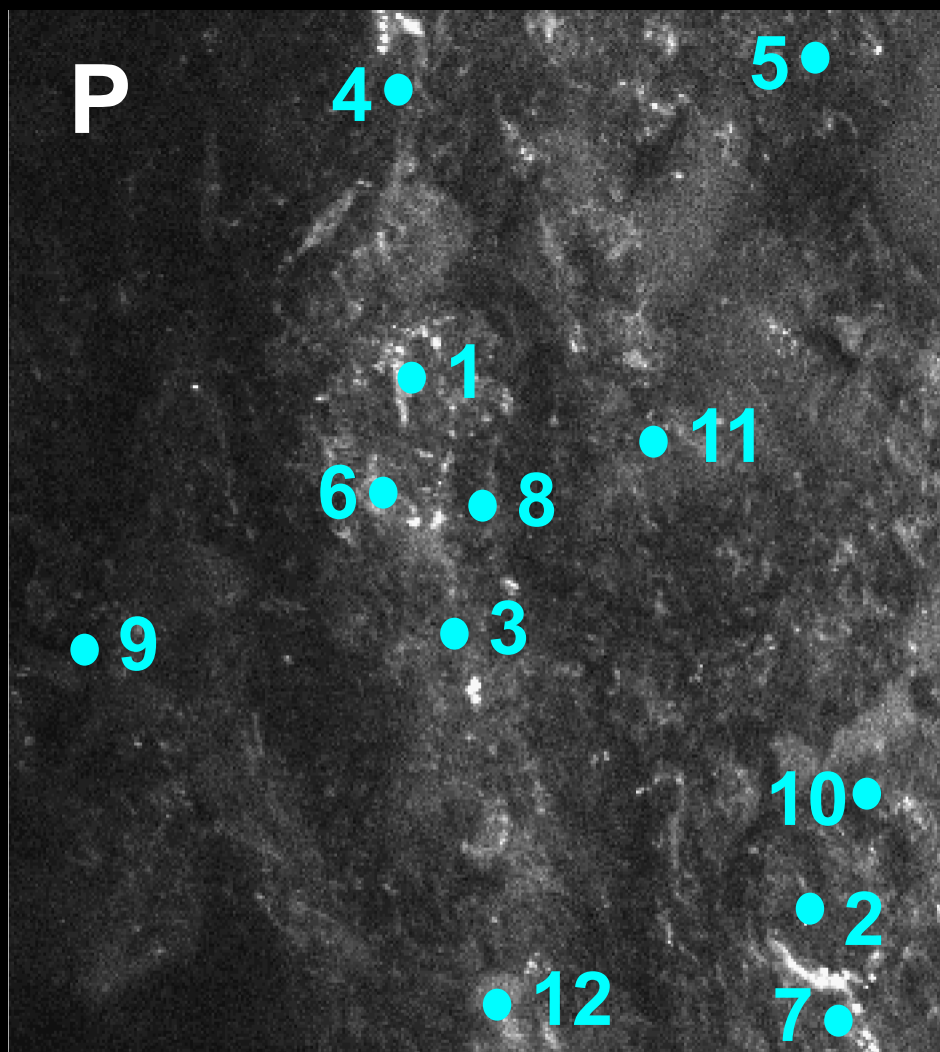
50  $\mu\text{m}$

# PHOSPHORUS AND ALUMINUM MAPS



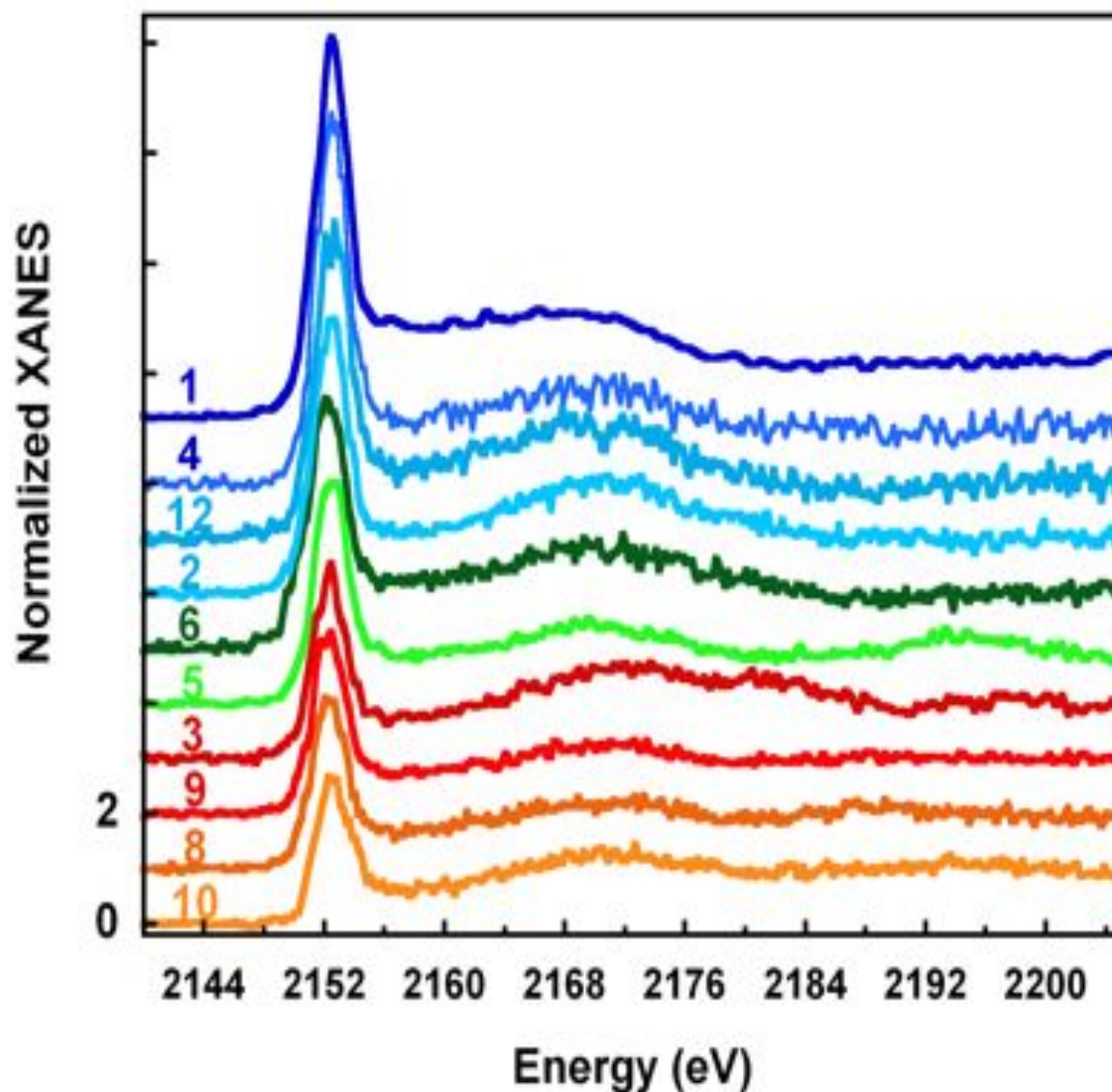
50  $\mu\text{m}$

# PHOSPHORUS AND ALUMINUM MAPS



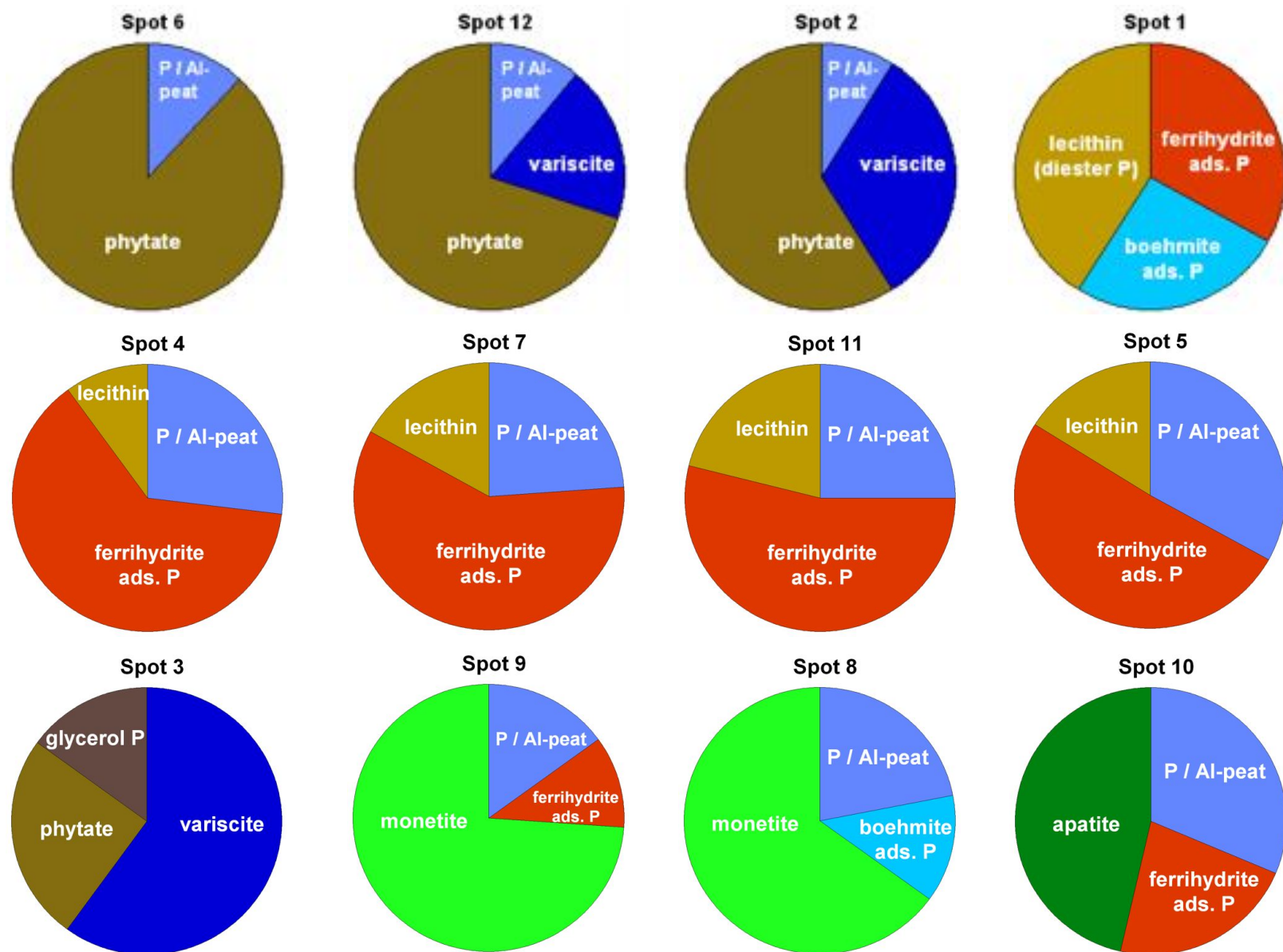
50  $\mu\text{m}$

## Diversity of P K-edge XANES spectra within a 50 x 50 $\mu\text{m}$ area of organic soil material



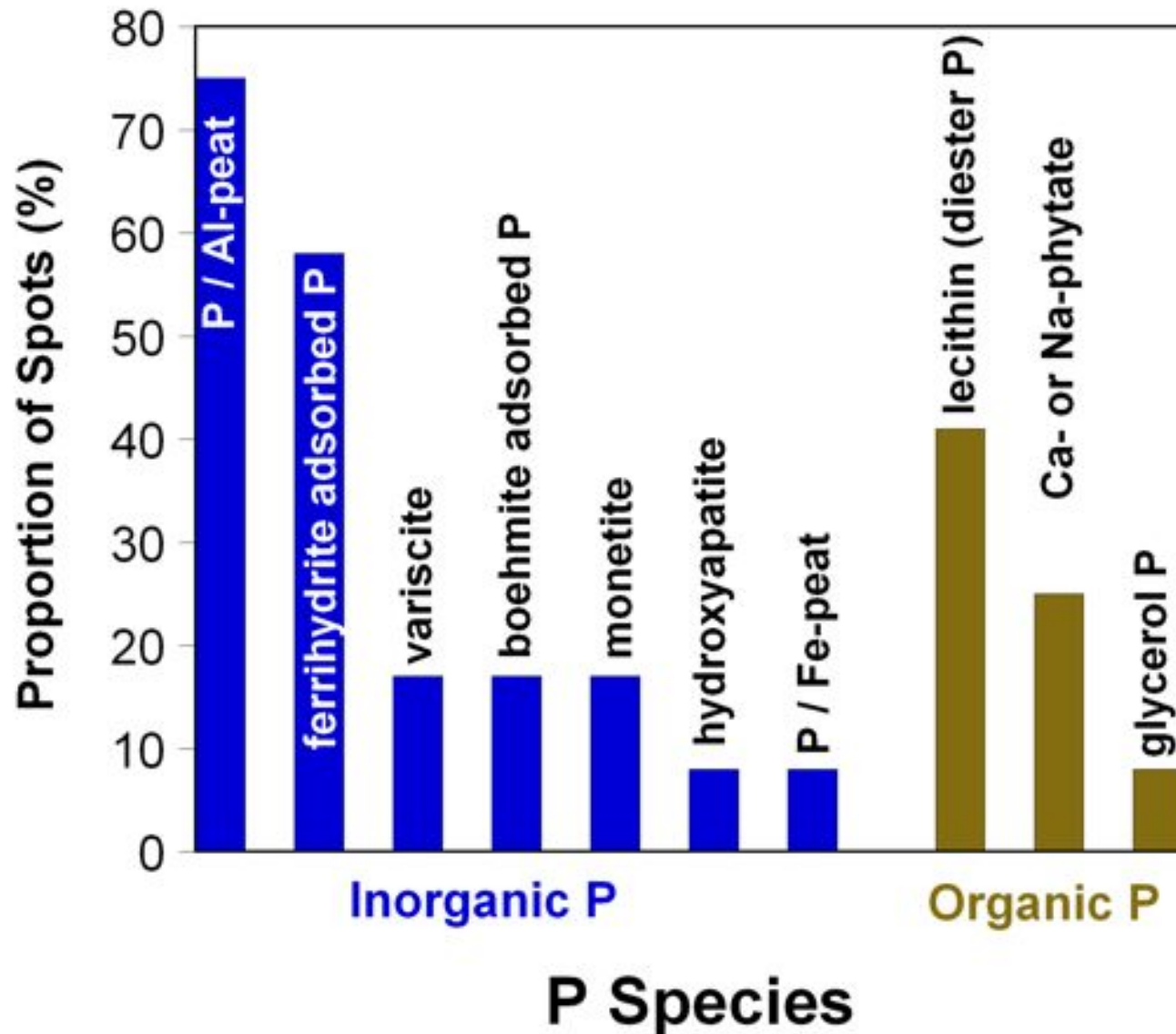


# Overall P Species Distribution (50 x 50 $\mu\text{m}$ Sample Region)



Fits to P XANES spectra in 50 x 50  $\mu\text{m}^2$  region included ten standards.

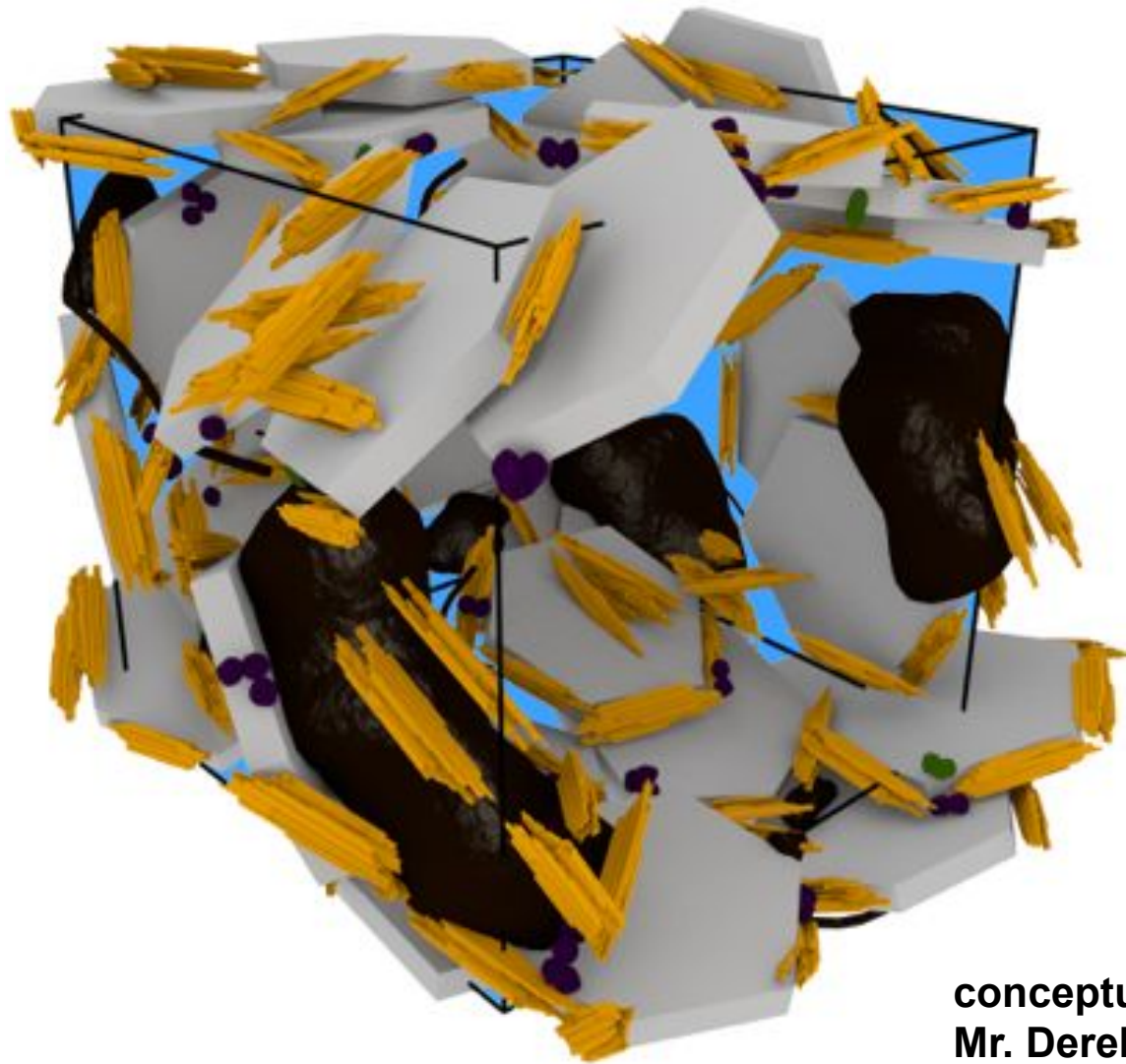
How mobile is phosphorus in this soil?



# THE REACTIVE MICROSITE MODEL

**Hypothesis: Need chemical speciation AND geochemical microenvironment properties to predict mobility**

1  $\mu\text{m}^3$



conceptual model drawn by  
Mr. Derek Elliot

A close-up photograph of a rock face. A vertical crack runs down the center, and a horizontal crack runs across the middle. A dashed line is drawn across the rock face, indicating a potential failure plane.

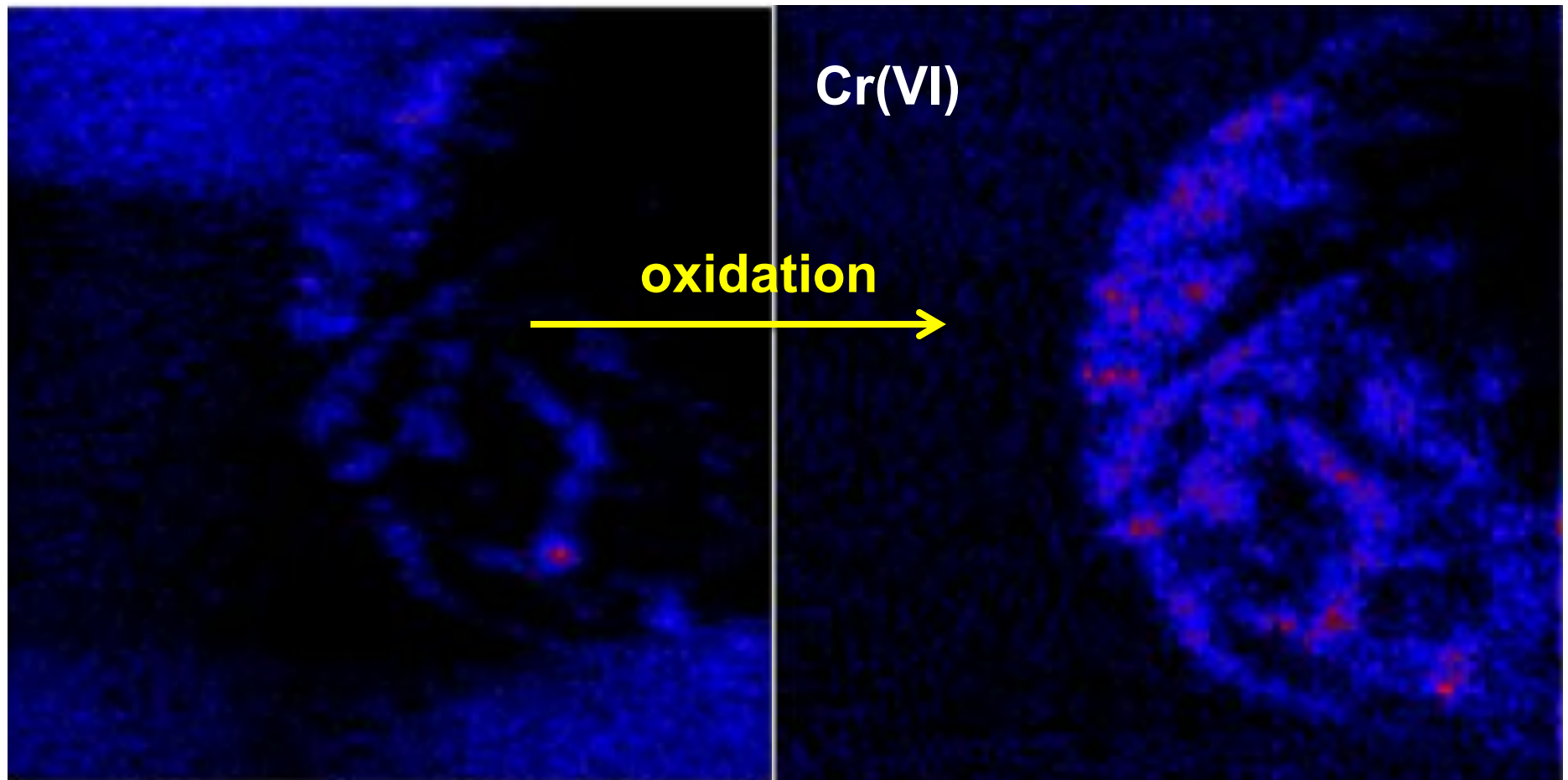
The diagram illustrates the complex geochemical behavior of Cr(III) in a pore water environment. The central blue circle represents the **PORE WATER**. Various processes are shown as arrows connecting different chemical species and solid phases:

- Organic Matter (OM):** At the top, a dark brown irregular shape represents OM. Arrows show **complexation** between OM and  $\text{Cr(III)}$ , and **adsorption** of  $\text{DOM}$  (Dissolved Organic Matter) onto the pore water boundary.
- Iron Cycle:** On the left, a yellowish-brown crystalline structure represents **Fe(III) (hydr)oxide**. Arrows show **reduction** of  $\text{Fe(III)}$  to  $\text{Fe(II)}$  in the pore water, and **(ad)sorption** of  $\text{HCrO}_4^-$ ,  $\text{Al(III)}$ , and  $\text{DOM}$  onto the iron oxide surface.
- Manganese Cycle:** At the bottom, a dark purple irregular shape represents **Mn(III,IV) oxide**. Arrows show **Cr(III) oxidation** to  $\text{HCrO}_4^-$  and  $\text{Mn}^{2+}$  in the pore water.
- Aluminum Cycle:** On the right, a grey hexagonal structure represents **Al (hydr)oxide**. Arrows show **dissolution** of  $\text{Al(III)}$  into the pore water and **adsorption** of  $\text{HCrO}_4^-$  and  $\text{DOM}$  onto the aluminum oxide surface.
- Cr(III) Speciation and Interactions:**
  - $\text{Cr(III)}$  is shown in the pore water, with arrows indicating **precipitation** to form **Cr(III)-hydroxide** (a green cluster) and **dissolution** back into the pore water.
  - $\text{HCrO}_4^-$  is shown in the pore water, with arrows indicating **reduction** to  $\text{Cr(III)}$  and **adsorption** onto organic matter and iron/aluminum oxides.

**conceptual models drawn  
by Mr. Derek Elliot**



# MEASURING MICROSCALE SOIL REACTIVITY

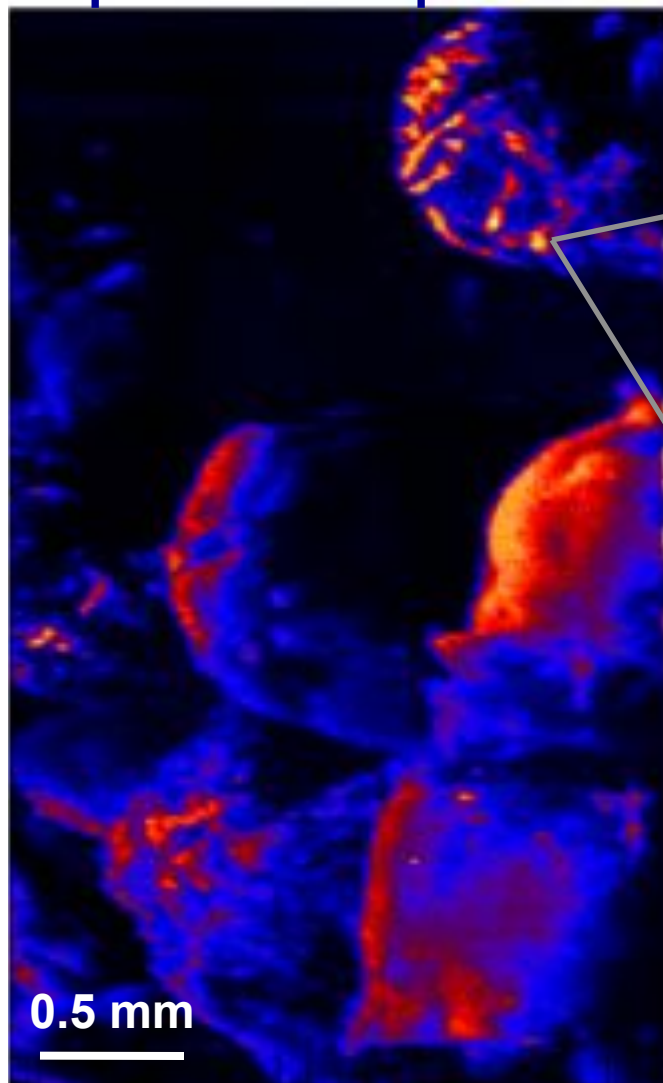


# **EXAMPLE**

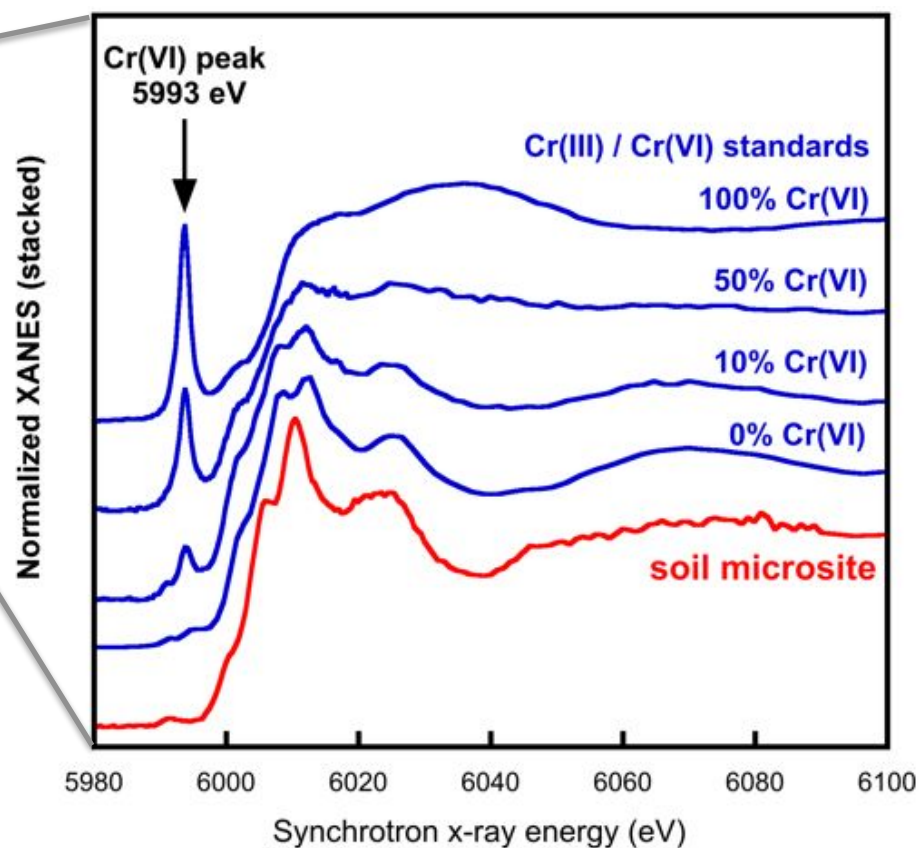
**OXIDATION OF NATURALLY OCCURRING CHROMIUM  
IN A SERPENTINIC SOIL**

# MICROSCALE Cr SPECIATION IN SERPENTINIC SOIL MATERIAL

Chromium distribution in  
serpentinic soil particles



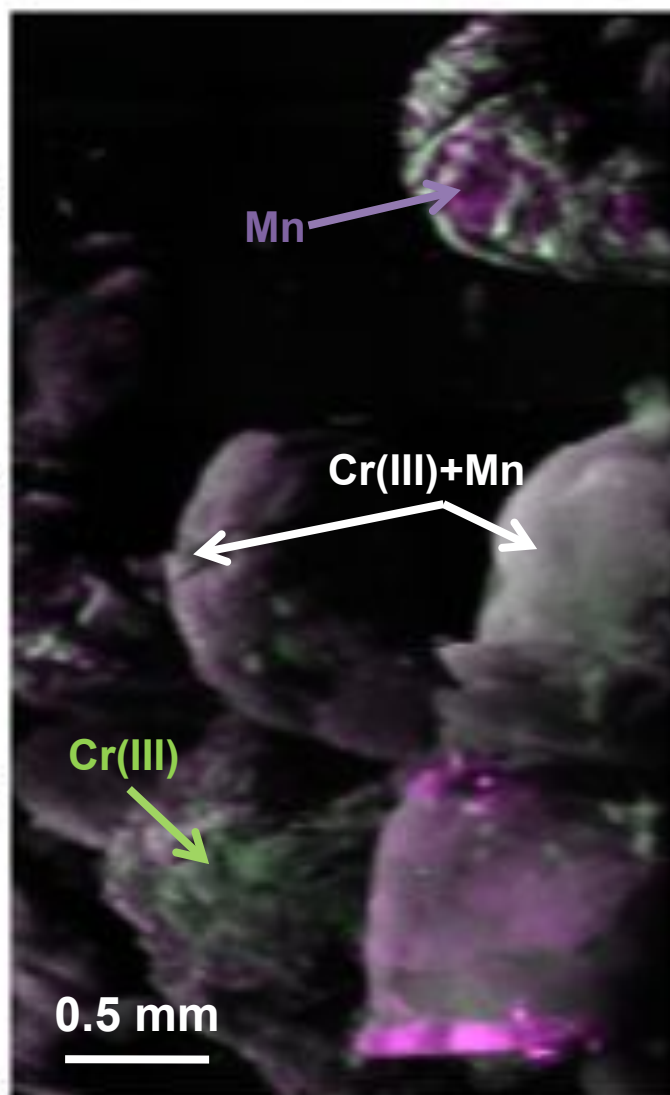
Chromium(VI) not detected by micro-  
XANES analysis of selected spots



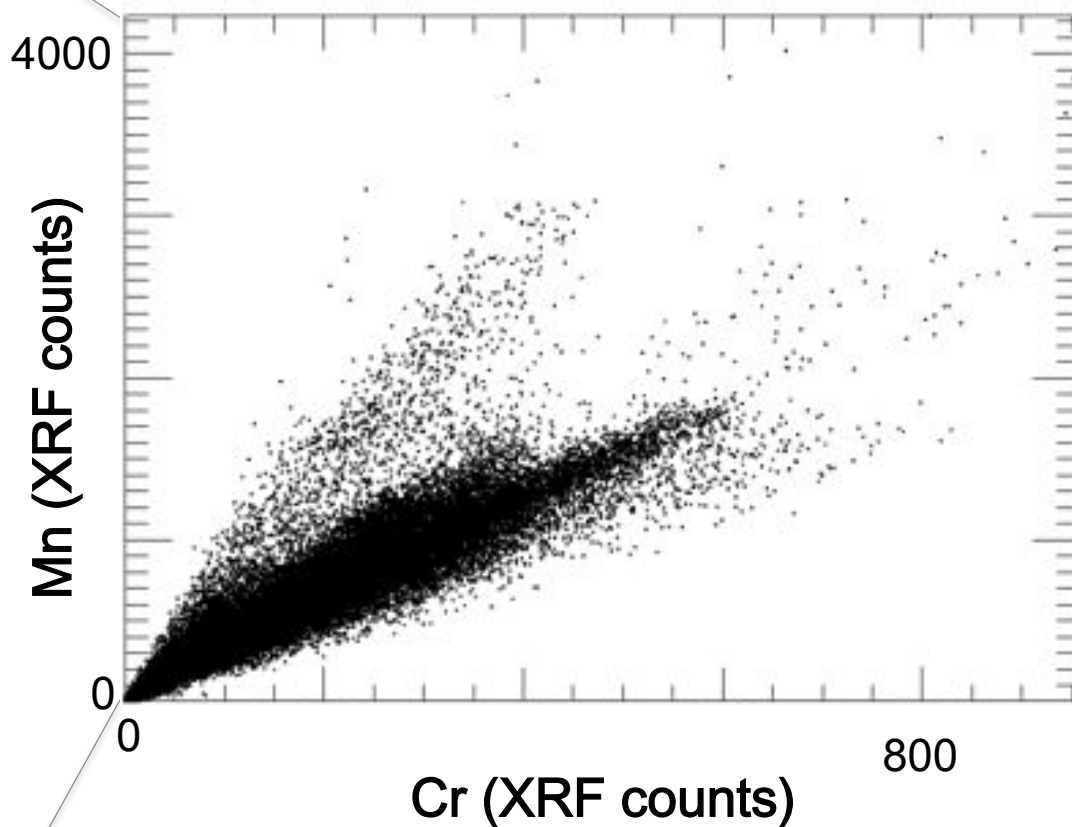
NSLS Beamline X27A (10 x 10  $\mu\text{m}$  resolution)

# GEOCHEMICAL MICROENVIRONMENT PROPERTIES OF SOIL MATERIAL

Co-localization of chromium and manganese (known redox couples)



Simple correlation

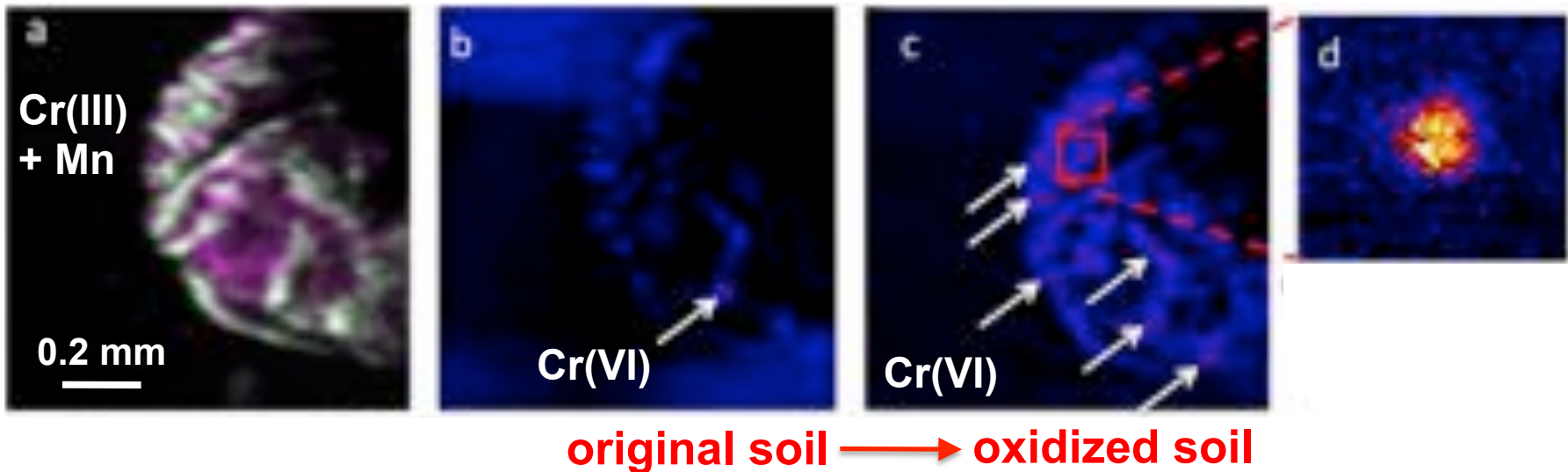


NSLS Beamline X27A (10 x 10  $\mu\text{m}$  resolution)



# MICROSCALE CHEMICAL REACTIVITY

**Cr(III) oxidation to Cr(VI) by  $\text{H}_2\text{O}_2$  is not uniform.  
Is it related to geochemical microenvironments?**



NSLS Beamline X27A (10 x 10  $\mu\text{m}$  resolution)

# **EXAMPLE**

**ARSENIC ACCUMULATION IN SOIL SAND GRAIN  
COATINGS TREATED WITH ARSENIC(III)**

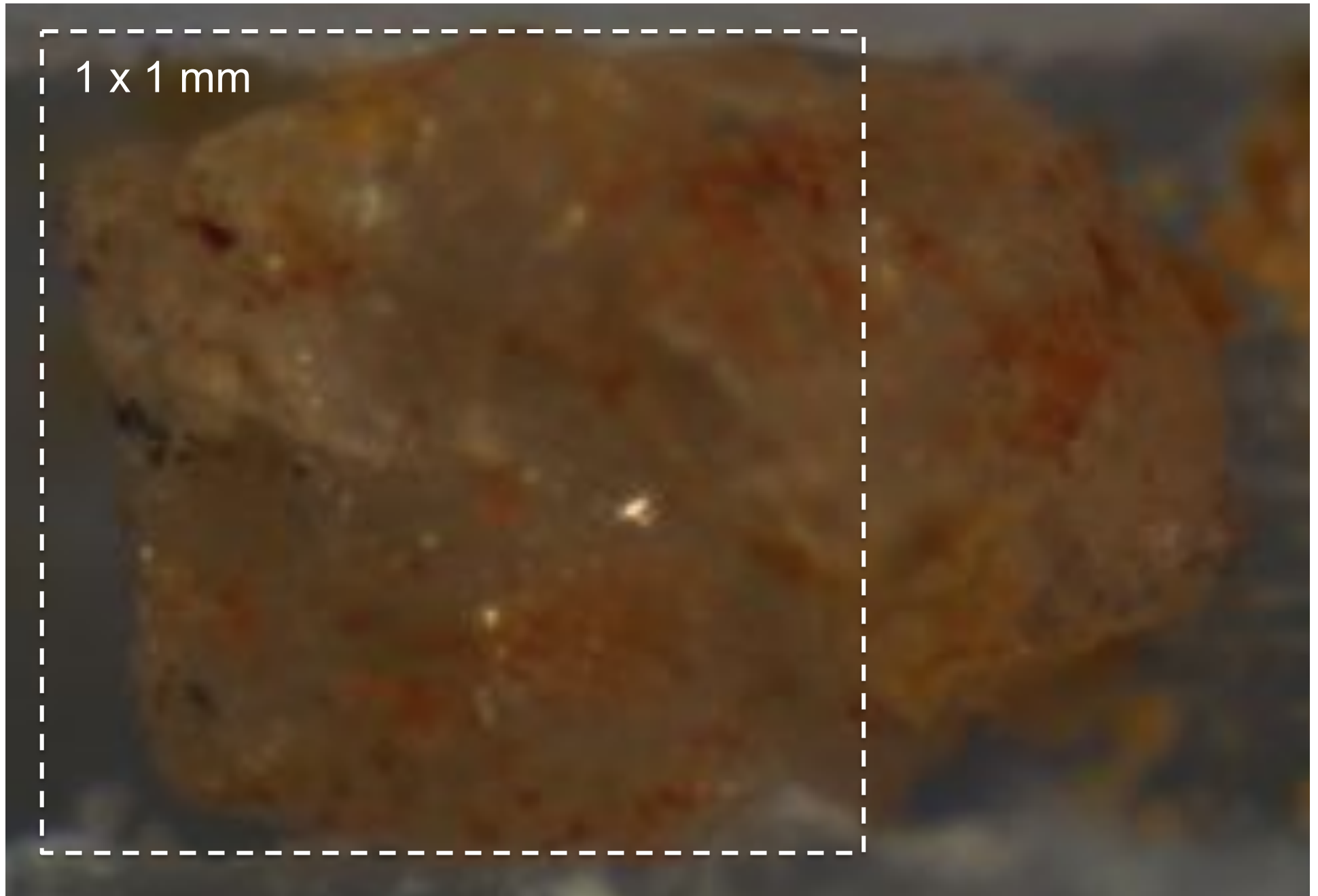




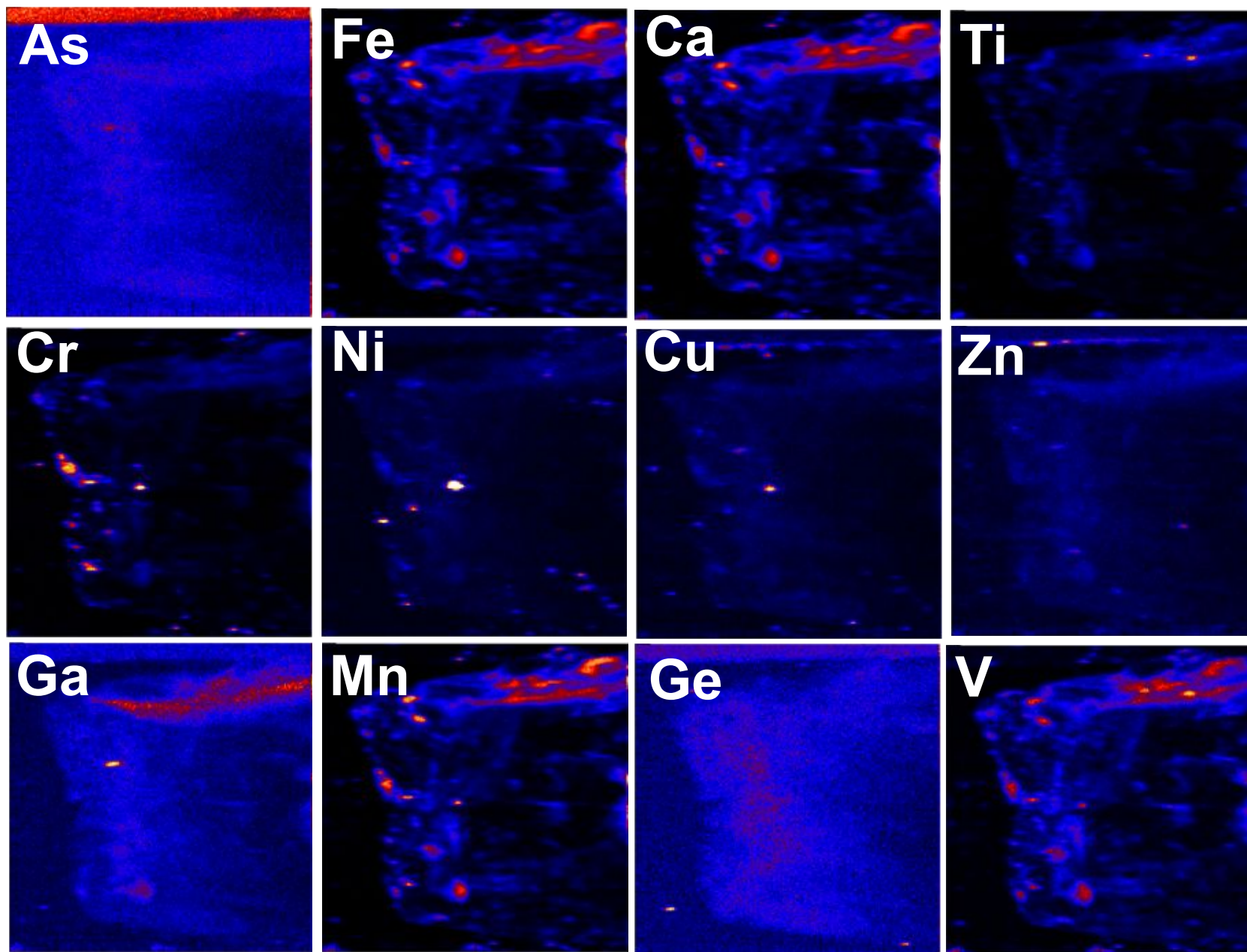




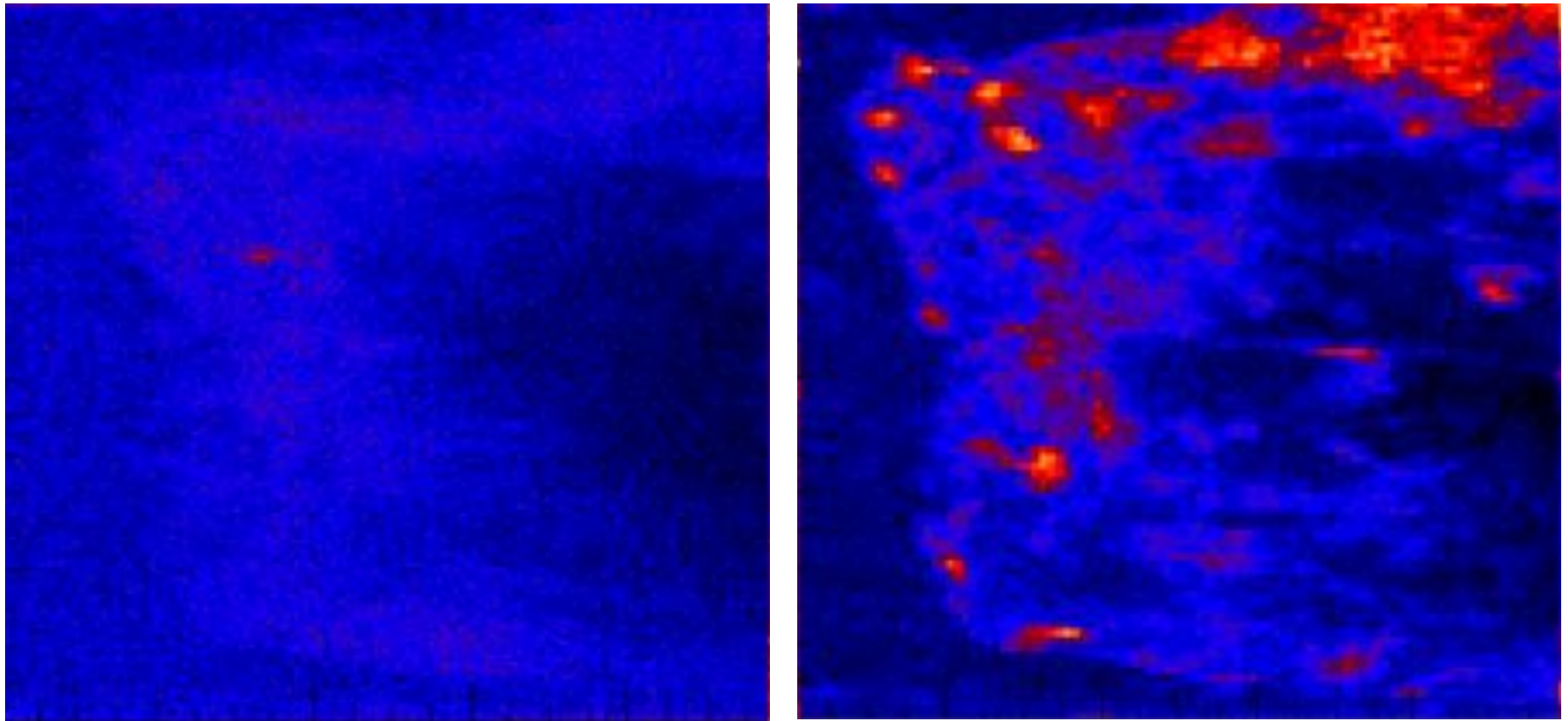
# LIGHT MICROSCOPE IMAGE OF SAND GRAIN



# X-ray fluorescence maps (12 keV – 1 x 1 mm<sup>2</sup>) from Original Sand Grain

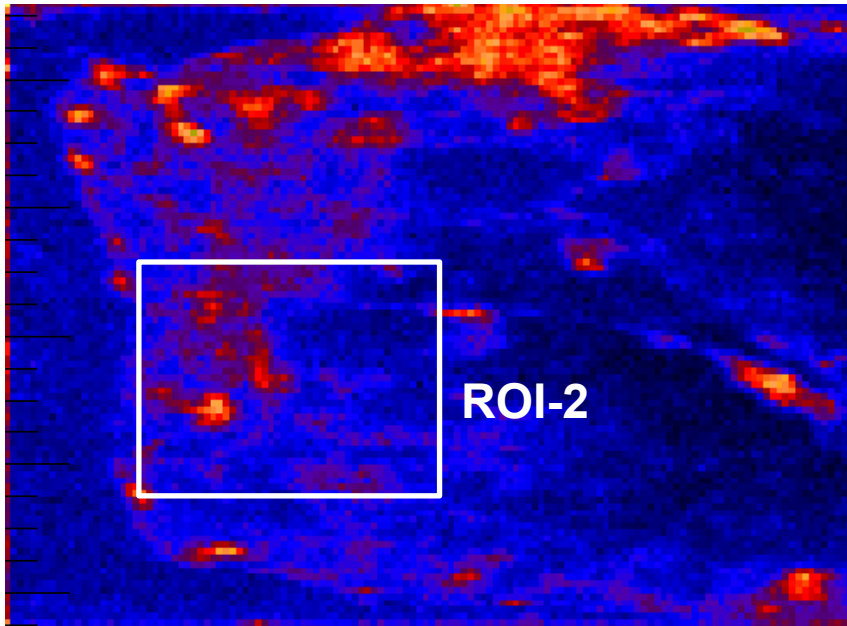


# Arsenic Distributions before and after treatment with As(III) as 0.1 mM $\text{Na}_2\text{AsO}_2$

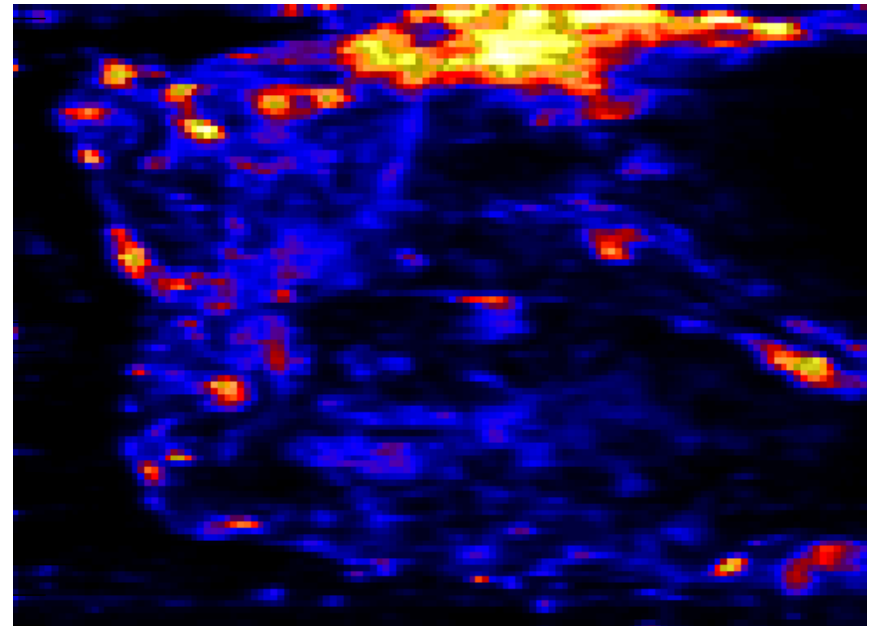


# Arsenic distribution is similar to Fe distribution

**As (total)**



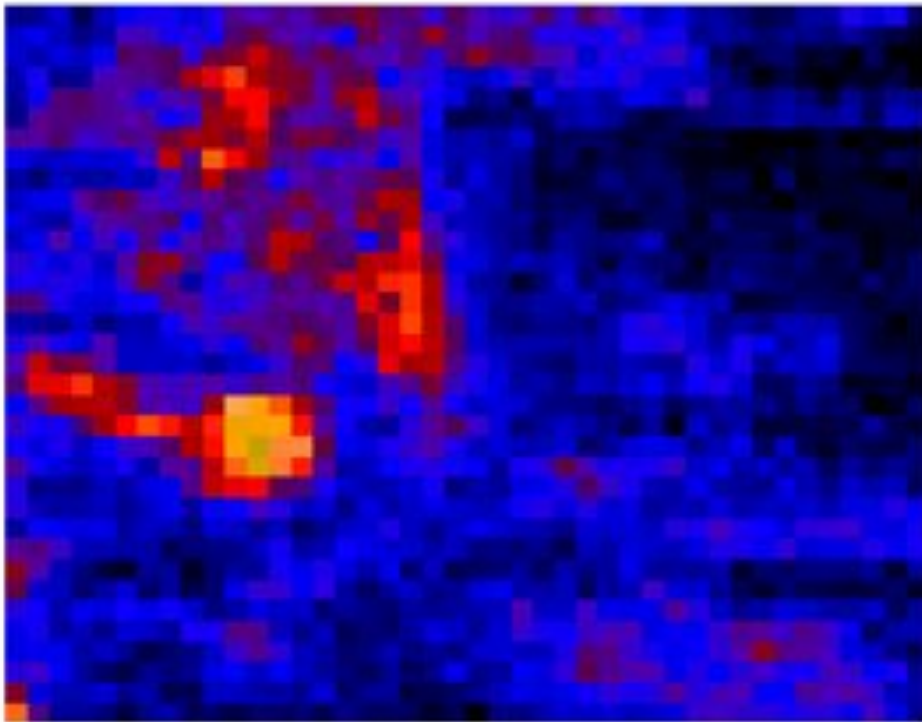
**Fe**



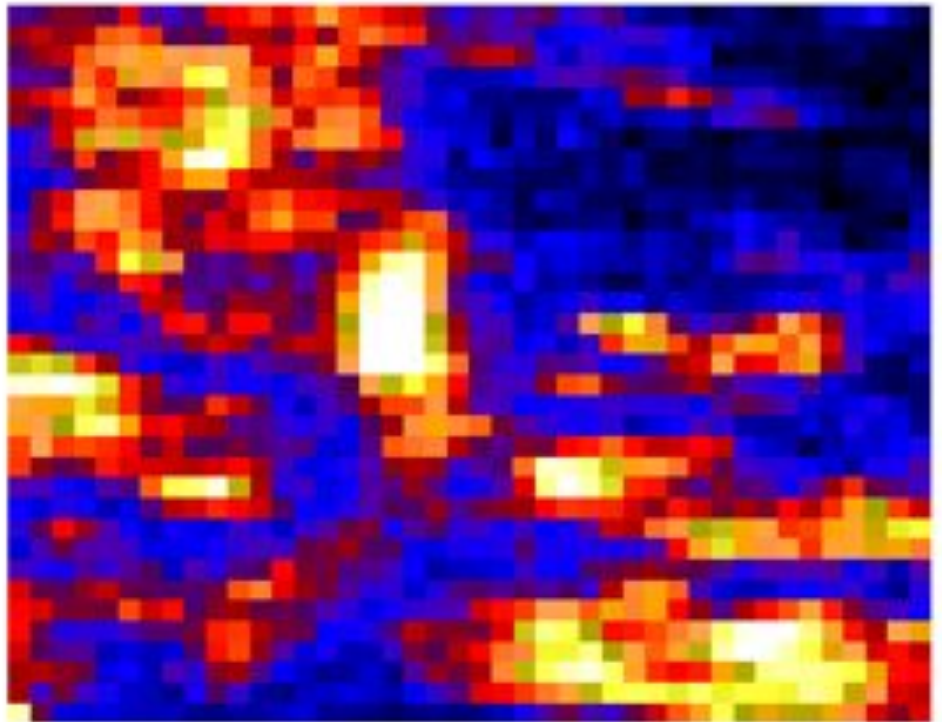


**X-ray fluorescence map (12 keV) of ROI-2 after sequential As(III) treatments 1 and 2 (450 x 350  $\mu\text{m}$  image; 10 x 10  $\mu\text{m}$  pixels)**

**After Treatment 1  
(0.1 mM NaAsO<sub>2</sub> sol'n)**

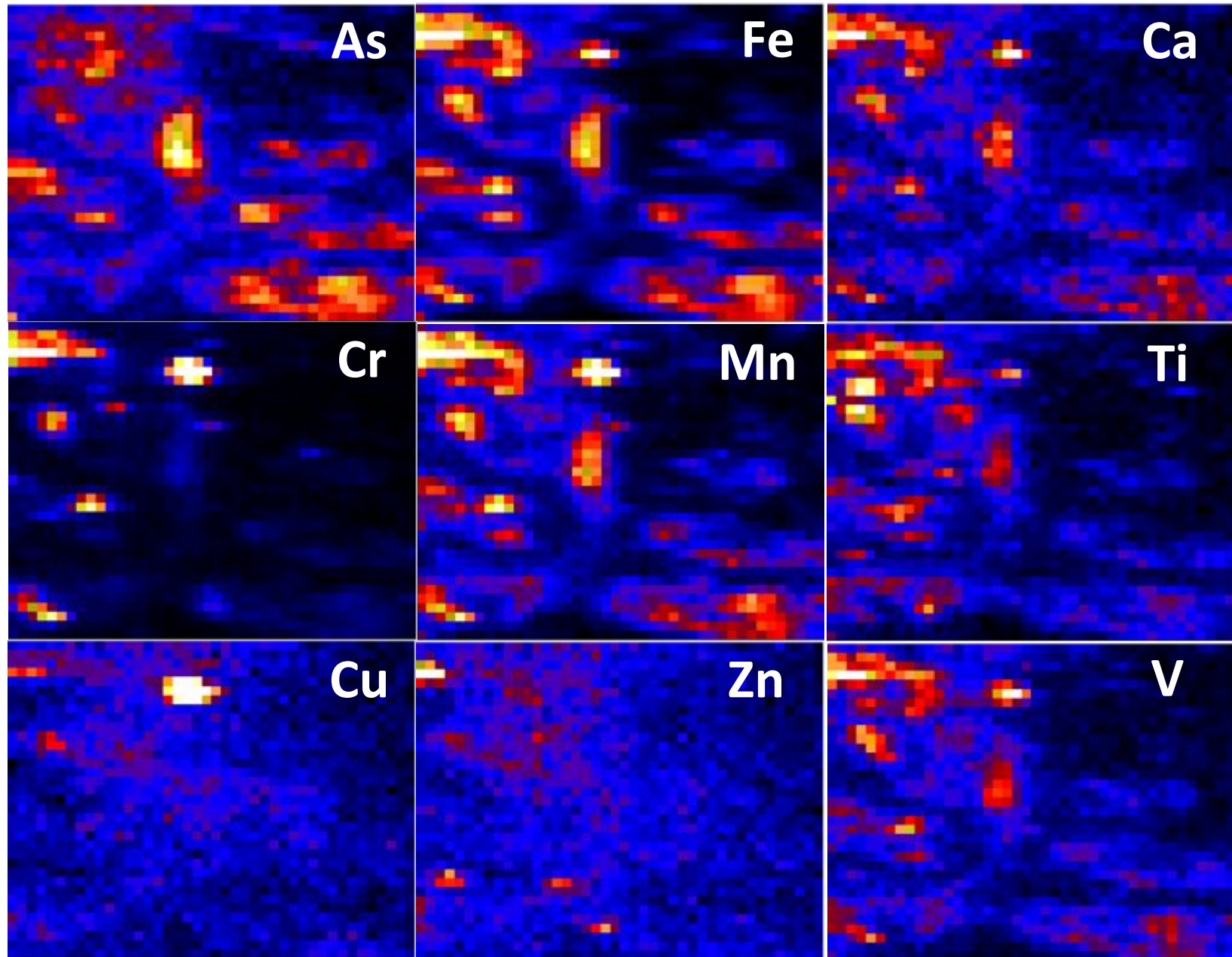


**After Treatment 2  
(1 mM NaAsO<sub>2</sub> sol'n)**



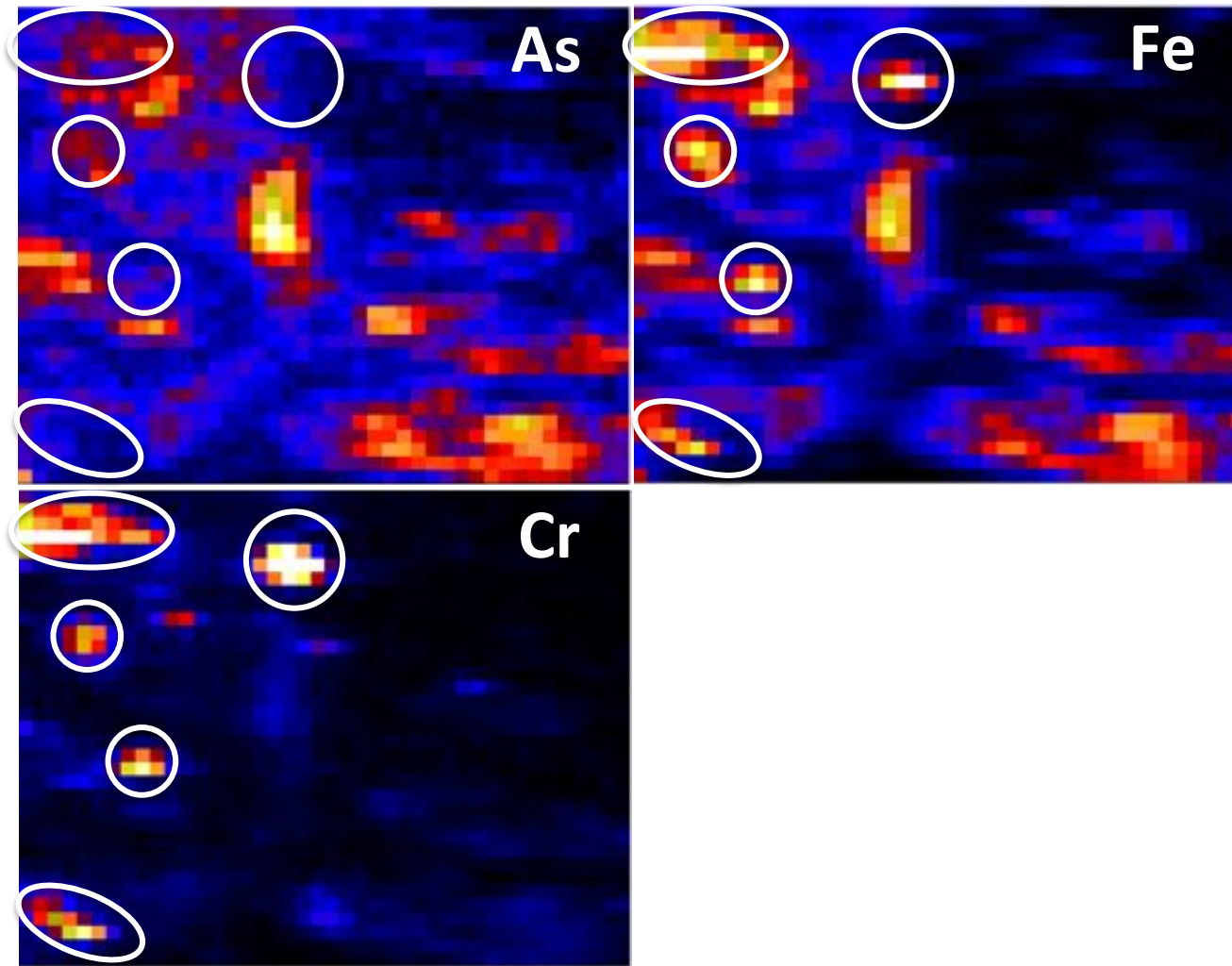
**Count range = 84 - 500**

## Arsenic in ROI-2 after two As(III) treatments



P1E0\_6As3\_2Rad1b\_NAV\_ROI2

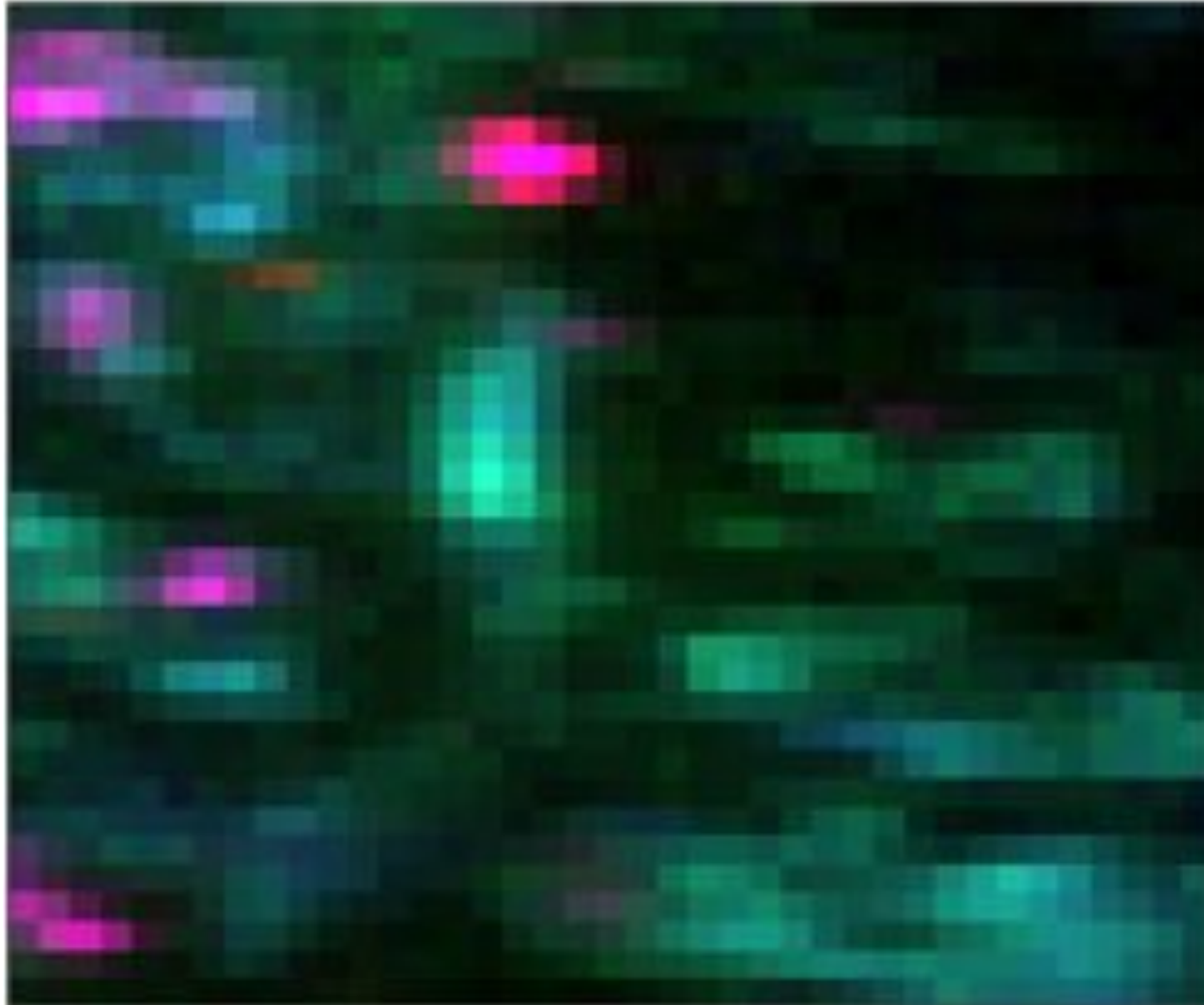
**Arsenic accumulation appears to be diminished in areas of high Cr + high Fe**





Color blended map with Cr (red), As (green), and Fe (blue)

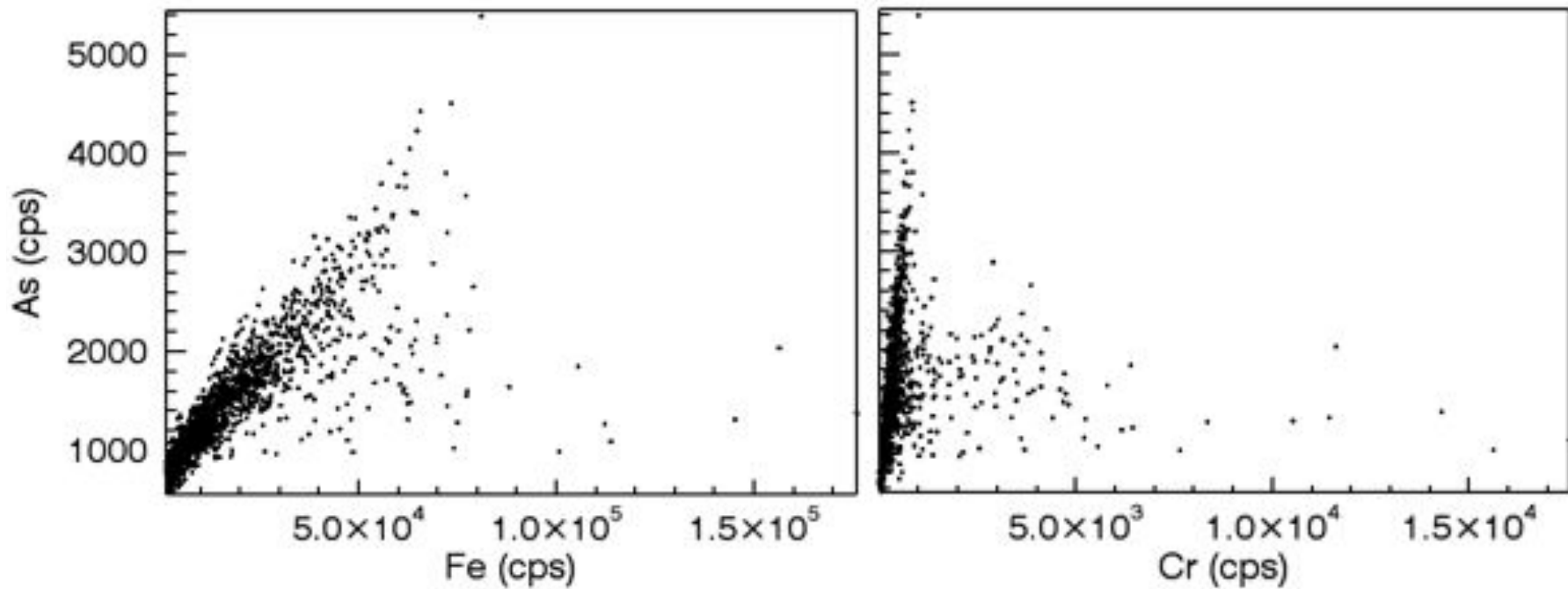
Purplish: Fe +Cr    Orangish: Cr + As (lower Fe)    Bluish-green: Fe +As



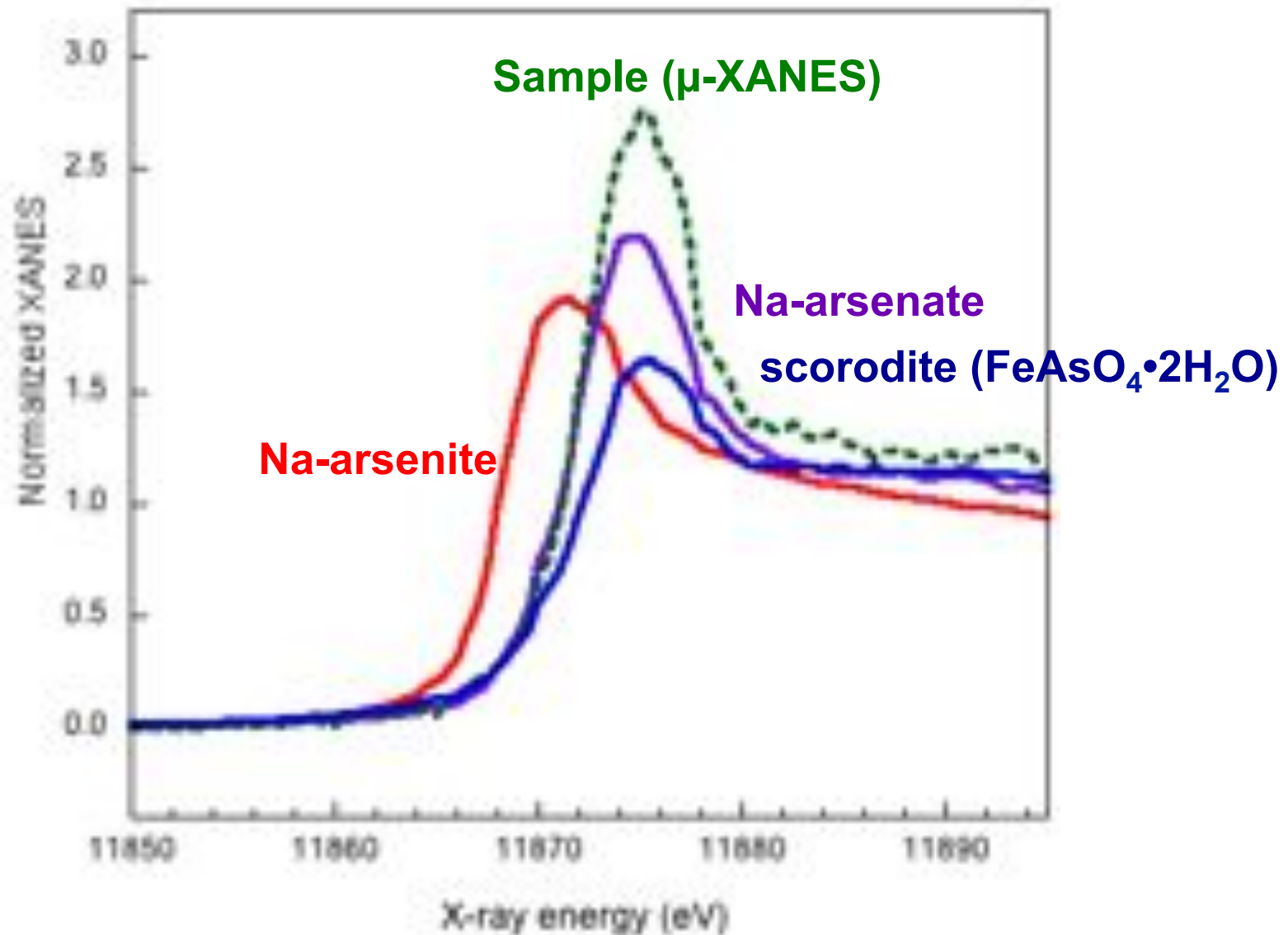
P1E0\_6As3\_2Rad1b\_NAV\_ROI2



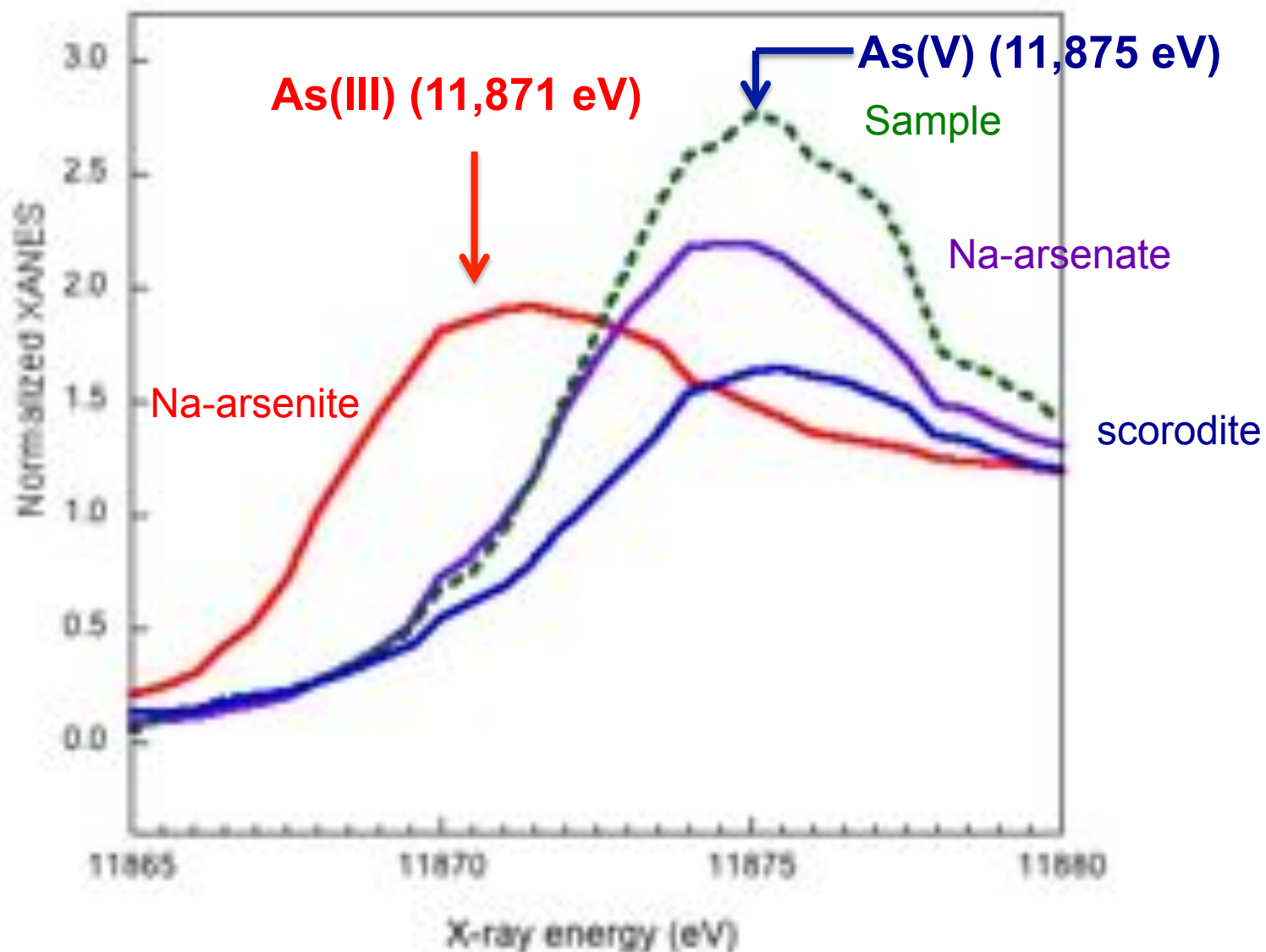
## Simple correlation plots of As vs. Cr or Fe in ROI-2



**Selected As K-edge micro-XANES spectra (after 1<sup>st</sup> As treatment)  
indicated that As(III) largely oxidized to As(V)**



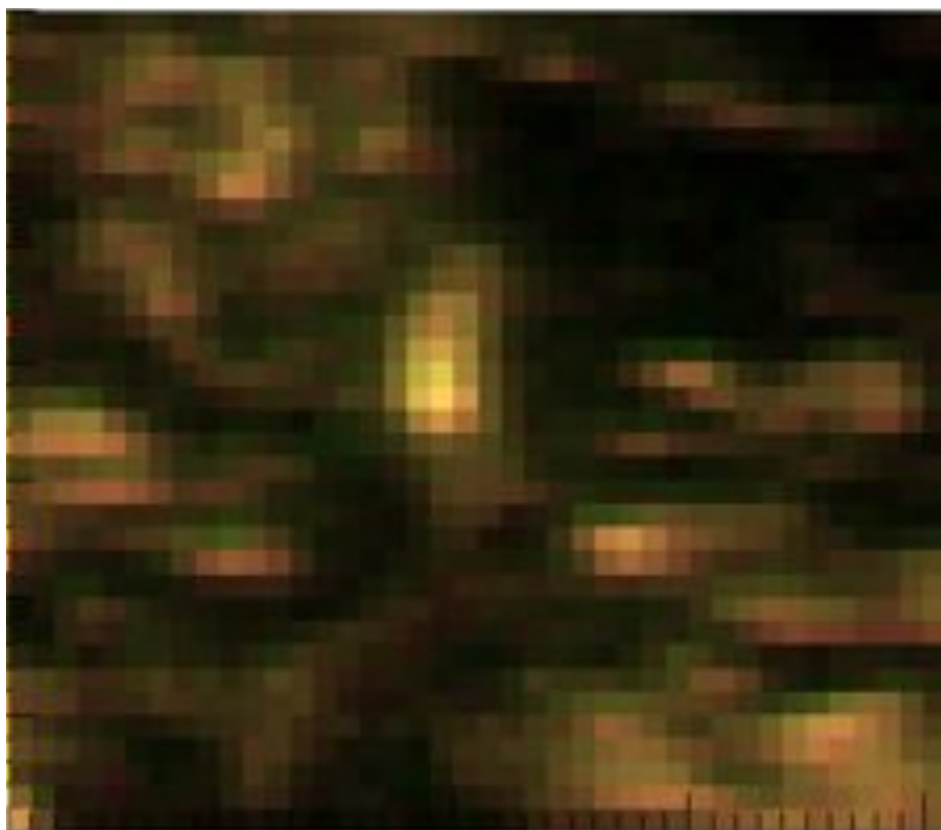
**XANES maps collected over larger area, but narrower energy range after 2<sup>nd</sup> As(III) treatment**



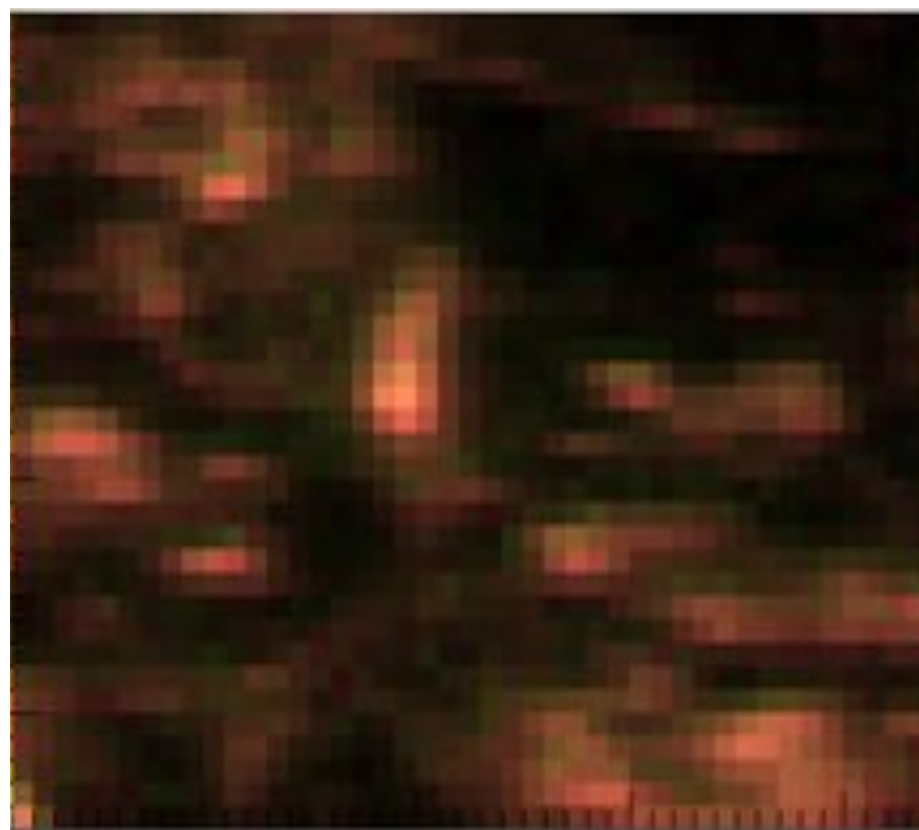
# Evidence for UV-visible light-induced oxidation of As(III) to As(V) (1 hour radiation treatment of wet sample)

As(III) = Green + Blue      As(V) = Red

**BEFORE**



**AFTER**

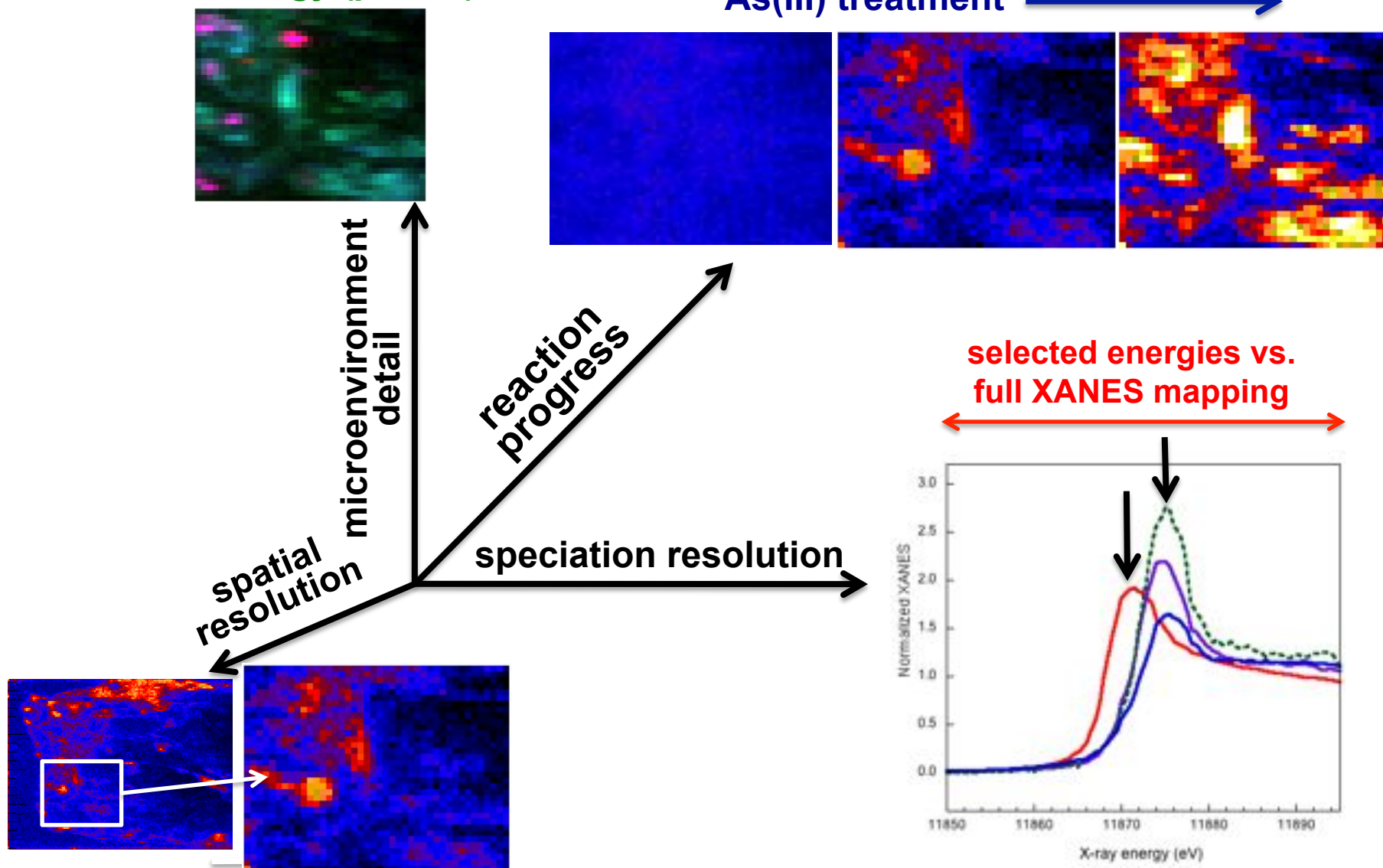




# NEED TO EXPAND AND OPTIMIZE CHARACTERIZATION PARAMETERS

microsite composition ( $\mu$ -XRF)  
speciation (XANES mapping)  
mineralogy ( $\mu$ -XRD)

As(III) treatment  $\longrightarrow$



# **ADVANTAGES OF THE XRS FOR MICROREACTIVITY RESEARCH – IN PRIORITY ORDER**

## **1. VARIABLE SPATIAL RESOLUTION**

**SURVEY (high flux) and DETAIL (high resolution)**

**- Can we get stronger element correlations with greater resolution?**

## **2. WIDE ENERGY RANGE (in conjunction with XFN)**

**As ---> Fe, Mn, S, C (+Al and other trace elements)**

**Cr ---> Mn, Fe, S, C (+ Fe, Al and other trace elements)**

## **3. HIGH FLUX**

**Need faster XANES mapping of low-concentration elements**

## **4. X-RAY MICRODIFFRACTION CAPABILITIES**

**What structures contain the elements that affect transformations?**

## **5. X-RAY TOMOGRAPHY**

**Can thickness of grain coatings on particles be measured?**



# **ACKNOWLEDGMENTS**

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- **Ms. Kimberly Hutchison (NC State – Soil Sci.)**
- **Dr. Martine Duff (Savannah River Site)**
- **Dr. Joe B. Dixon (Texas A&M)**
- **Dr. Michael J. Vepraskas (NC State – Soil Sci.)**
- **Beamline X-27A at the National Synchrotron Light Source and 2-IDB at the Advanced Photon Source, supported by DOE's Divisions of Materials Science and Chemical Sciences**